CATALYTIC PYROLYSIS CONVERSION OF LIGNIN FROM DIFFERENT SOURCES TO PHENOLS

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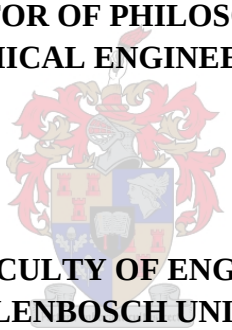

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ABSTRACT

Lignin is a by-product of the paper and pulp industry and the emerging cellulosic ethanol production technologies. Both industries only considered lignin a source of energy to complement the energy needs of their processes. However, the phenolic nature of lignin makes it a valuable renewable resource for sustainable production of chemical products.

In the current study, prior to lignin conversion to phenolic chemical products, physico-chemical characterisation of several lignins were conducted using conventional methods namely, wet chemical, gel permeation chromatography (GPC), and Fourier transform infra-red spectroscopy (FTIR). In addition to these methods, a novel analytical pyrolysis method was developed combining thermogravimetric analysis (TGA), thermal desorption (TD), and gas chromatography coupled to mass spectrometry (GC-MS), named as TGA-TD-GC-MS. It was used to analyse and estimate the monomeric phenolic products namely, syringol (S), guaiacol (G) and phenol (H) from lignins. The phenolic monomeric proportions (S/G/H), obtained using the TGA-TD-GC-MS was compared with the ones obtained by thioacidolysis (wet chemical method). The lignin monomeric products obtained by pyrolysis, based on internal calibration, was in the range of 5.5-12.9 wt.%. The ability of the TGA-TD-GC-MS to break several types of bonds gave it the advantage over thioacidolysis, resulting in the production of monomeric phenolic compositions that were more representative of the lignin.

A comparison of phenols production from catalytic pyrolysis of lignins of different biomass origin, namely eucalyptus (hardwood) lignin, pine (softwood) lignin, and sugarcane bagasse (herbaceous) lignin was studied using the TGA-TD-GC-MS. The lignins were impregnated with two hydroxides (NaOH and KOH) and two metal oxides (ZnO, and Al_2O_3), with amounts equivalent to 1 wt.% of the lignin mass, and pyrolysed at the temperature of 600 $^{\circ}$C using a heating rate of 10 $^{\circ}$C/min. KOH produced the most catalytic effect on the yield of total phenols from sugarcane bagasse (S-S) lignin, leading to the highest increase of +26%,

and likewise NaOH for eucalyptus (E-K) lignin (+40%). Syringol yield being the major syringol-type (S-type) phenols reached a record high of 1.8 wt.%, equivalent to 90% increase from E-K lignin, catalysed by NaOH. Additionally, NaOH increased the yield of 4-vinylguaicol-the guaiacol-type (G-type) phenol from E-K lignin up to 2.8 wt.%, equivalent to 39% increase, as compared to the non-catalytic yield.

A catalyst screening study was conducted in which twelve catalysts, namely Al_2O_3, Fe_2O_3, MoO_3, TiO_2, Ni/Al_2O_3-SiO_2, CaO, ZnO, MgO, NaOH, CuO, KOH and NiO were each impregnated on three different types of sugarcane bagasse lignins with amounts equivalent to 1 wt.% of the lignin mass. KOH, CaO, and Fe_2O_3 recorded the highest effects on the total yield of phenols from soda (SD), soda-anthraquinone (SAQ), and steam explosion combined with enzymatic hydrolysis lignins respectively. The increases were 11.2 wt.%, 8.2 wt.%, and 8.6 wt.%, equivalent to + 26%, + 60% and + 43% respectively. Syringol, guaiacol, and 4-vinylguaiacol were the most improved with yield increases ranging from 0.6 to 2.8 wt.%, equivalent to 32-121% from the lignins.

Optimisation of phenols was investigated. Pyrolysis was first conducted at analytical scale and then applied in the second stage at bench scale. The results at analytical scale showed that the amounts of KOH required to maximise the yield of phenols (15.3-16.0 wt.%) were in the range of 5-7 wt.%. Analysis of the bio-oil showed that the yields of syringol and guaiacol had their maximum values at 450 $^{\circ}$C and 4.5 wt.% KOH content with yield increases of 0.70 wt.% and 0.6 wt.%, which represent 106% and 83% respectively, compared with that of pyrolysis without catalyst. Phenol (the P-type phenol) achieved a maximum at 450 $^{\circ}$C and 8.5 wt.% KOH content, with a yield of 0.96 wt.%, corresponding to 141% increase.

OPSOMMING

Lignien is ’n byproduk van die papier- en pulpindustrie en die opkomende sellulosiese etanolproduksie-tegnologieë. Beide industrieë beskou lignien slegs as ’n bron van energie om die energiebenodigdhede van hul prosesse te komplimenteer. Die fenoliese natuur van lignien maak dit egter ’n waardevolle herwinbare hulpbron vir volhoubare produksie van chemiese produkte.

In die huidige studie, voor die lignien omskakeling na fenoliese chemiese produkte, is fisikochemiese karakterisering van verskeie ligniene verrig deur konvensionele metodes te gebruik, naamlik nat chemiese, jel deurlating chromatografie (GPC), en Fourier transform infrarooi spektroskopie (FTIR). Buiten hierdie metodes is ’n nuwe analitiese pirolise metode ontwikkel wat termogravimetriese analise (TGA), termodesorpsie (TD), en gaschromatografie gekoppel aan massa spektrometrie (GC- MS) kombineer, genaamd TGA-TD-GC-MS. Dit is gebruik om die monomeriese fenoliese produkte, syringol (S), guajakol (G) en fenol (H) van ligniene, te analiseer en beraam. Die fenoliese monomeriese proporsies (S/G/H), verkry deur die TGA-TD-GC-MS te gebruik, is vergelyk met dié verkry deur thioacidolysis (nat chemiese metode). Die lignien monomeriese produkte verkry deur piroliese, gebaseer op interne kalibrering, was in die bestek van 5.5–12.9 wt.%. Die vermoë van die TGA-TD-GC-MS om verskeie tipes bindings te breek, gee dit die voordeel oor thioacidolysis, wat die produksie van monomeriese fenoliese komposisies wat meer verteenwoordigend is van die lignien, tot gevolg het.

’n Vergelyking van fenolproduksie van katalitiese pirolise van ligniene van verskillende biomassa oorsprong, naamlik eukaliptus- (hardehout) lignien, den- (sagtehout) lignien, en suikerriet bagasse- (kruidagtig) lignien is bestudeer deur die TGA-TD-GC-MS te gebruik. Die ligniene is geïmpregneer met twee hidroksiedes (NaOH en KOH) en twee metaaloksiedes (ZnO en Al_2O_3) met hoeveelhede ekwivalent aan 1 wt.% van die lignien

massa, en gepiroliseer by ’n temperatuur van 600 °C deur ’n verhittingstempo van 10 °C/min te gebruik. KOH het die grootste katalitiese effek op die opbrengs van totale fenol uit suikerriet bagasse (S-S) lignien gehad, wat tot die hoogste verhoging van +26% gelei het, en ook NaOH vir eukaliptus- (E-K) lignien (+40%). Syringol-obrengs, wat die grootste syringol-tipe (S-tipe) fenol is, het ’n rekord hoogte van 1.8 wt.%, ekwivalent aan 90% verhoging van E-K-lignien gehad, gekataliseer deur NaOH. Boonop het die NaOH die opbrengs van 4-vinielguajakol-tipe (G-tipe) fenol van E-K-lignien verhoog tot en met 2.8 wt.%, ekwivalent tot 39% verhoging, in vergelyking met die nie-katalitiese opbrengs.

’n Katalis siftingstudie is uitgevoer waarin twaalf kataliste, genaamd Al_2O_3, Fe_2O_3, MoO_3, TiO_2, Ni/Al_2O_3-SiO_2, CaO, ZnO, MgO, NaOH, CuO, KOH en NiO elk geïmpregneer is op drie verskillende tipes suikerriet bagasse ligniene met hoeveelhede ekwivalent aan 1 wt.% van die lignien massa. KOH, CaO en Fe_2O_3 het die hoogste effek op die totale opbrengs van fenol uit soda (SD), soda-antrakinoon (SAQ), en stoomontploffing gekombineerd met ensimatiese hidrolise ligiene, onderskeidelik, aangeteken. Die verhogings was 1.2 wt%, 8.2 wt.% en 8.6 wt.%, ekwivalent aan +26%, +60% en +43%, onderskeidelik. Syringol, guajakol en 4-vinielguajakol het die grootste verbetering getoon met opbrengsverhogings met ’n bestek van 0.6 tot 2.8 wt.%, ekwivalent aan 32–121% van die ligniene.

Optimering van fenol is ondersoek. Pirolise is eers uitgevoer op analitiese skaal en toe toegepas in die tweede fase by banktoetskaal. Die resultate op analitiese skaal het gewys dat die hoeveelhede KOH benodig om die opbrengs van fenol (15.3 – 16.0) te maksimeer, is in die bestek van 5–7 wt.%. Analise van die bio-olie het gewys dat die opbrengs van syringol en guajakol hul maksimum waardes het by 450 °C en 4.5 wt.% KOH inhoud met opbrengsverhogings van 0.70 wt.% en 0.6 wt.%, wat 106% en 83% onderskeidelik, verteenwoordig, in vergelyking met dié van pirolise sonder katalis. Fenol (die P-tipe fenol)

het ’n maksimum bereik by 450 °C en 8.5 wt.% KOH inhoud, met ’n opbrengs van 0.96 wt.%, ooreenstemmend met 141% verhoging.

Dedication

To my wife Vicky, who sacrificed a lot during this research journey.

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Lastly, to God almighty whom I serve always, may your will be done!

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Lists of Acronyms and Abbreviations

AQ	Anthraquinone
AHQ	Anthrahydroquinone
ATR	Attenuated total reflectance
ANOVA	Analysis of variance
ASTM	American standards for testing of materials
BHT	Butylated hydroxytoluene
BTX	Benzene, toluene, xylene
CEL	Cellulolytic enzyme lignin
DFRC	Derivatisation followed by reductive cleavage
DHBF	Dihydrobenzofuran
DMSO	Dimethylsulphoxide
DoE	Design of experiments
DTG	Derivative thermogravimetric
DTG_{max}	Maximum degradation rate
EI	Electron impact
E-K	Eucalyptus Kraft lignin
EMAL	Enzymatic mild acidolysis lignin
ESP	Electrostatic precipitator
FC	Fixed carbon
FPU	Filter paper unit
FTIR	Fourier transformed infra-red
GC/MS	Gas chromatography/mass spectrometry
GPC	Gel permeation chromatography
HPLC	High-performance liquid chromatography
HWD	Hardwood
IU	International unit
LCC	Lignin-carbohydrate complexes
MSW	Municipal solid waste
MWL	Milled wood lignin
NBO	Nitrobenzene oxidation

NIST	National institute for standards and technology
NMR	Nuclear magnetic resonance
NSSC	Neutral sulphite semi-chemical
PCA	Principal component analysis
PCR	Pyrolysis centrifuge reactor
P-K	Pine Kraft lignin
Py-GC-FID	Pyrolysis-gas chromatography-flame ionisation detection
Py-GC/MS	Pyrolysis-gas chromatography/mass spectrometry
RSD	Relative standard deviation
SAQ	Soda anthraquinone lignin
SEH	Steam explosion combined with enzymatic hydrolysis lignin
SD	Soda lignin
S/G/H	Syringyl/guaiacyl/hydroxyphenyl
S/G	Syringyl/guaiacyl ratio
S-S	Soda sugarcane bagasse lignin
SWD	Softwood
TG	Thermogravimetric
TD	Thermal desorption
TEA	Triethanolamine
THF	Tetrahydrofuran
TIC	Total ion chromatograms
TGA	Thermogravimetric analyser
TGA-TD-GC/MS	Thermo gravimetric analysis-thermal desorption gas chromatography-mass spectroscopy
TMSA	Trimethylsylilated with N,O-bis(trimethylsilyl) acetamine
UV	Ultra-Violet
VM	Volatile matter
WIS	Washed insoluble solid

CHAPTER ONE

INTRODUCTION

1.1. Contextual Background

The concerns over the effects of the exploration of fossil fuels on the environment have prompted the need to manufacture chemicals and fuels from alternatives, renewable and sustainable sources [1]. Among the alternatives, lignocellulosic biomass represents a boundless resource for the production of fuels and chemicals because it is readily available and relatively inexpensive compared to other types of plant biomass [2–6]. Lignocellulosic biomass is not in conflict with food, as it is non-edible [7]. Due to its renewability, lignocellulosic biomass can minimise the emissions of greenhouse gases [8], as the CO_2 emitted from their incinerations are absorbed during photosynthesis by plants [9,10]. Therefore, it is the preferred bio-resources to replace the non-renewable resources. Lignocellulosic biomasses include various agricultural residues, woods (deciduous and coniferous), municipal solid waste (MSW) namely, papers, cardboards, yard trashes, wood processing waste products, pulp and paper industry wastes, etc.

Among the processes exploiting lignocellulosic biomass materials, the production of pulp and paper or second generation bioethanol, are well-established to maximise cellulose and hemicellulose conversion to value-added products, while lignin (which constitutes up to 30 % of the total carbon contained on the planet's lignocellulosic biomass) is traditionally utilized for heat and power through combustion [5,11,12]. Although the utilisation of lignin for power generation and heat is economically viable in the near-term, it is essential that innovative technologies increase lignin's value to enhance the development of bio-refinery processes that maximise the economic benefits derived from lignocellulose[13,14].

Currently, most of the high value chemicals including phenols are produced from fossil fuels resources, as exemplified by the USA, which produces more than 90% of its phenolic chemicals from non-renewable resources [15]. However, lignin which originates from a renewable bio-resource is a potential alternative source of phenolic compounds. To date, there is a lack of efficient technology that can transform lignin into value added chemical products in the development of a biomass-based bio-refinery [16,17]. The reason is related to the complex and highly stable nature of lignin structure, which alternate with the diverse lignocellulosic biomass materials, and delignification methods used during fractionations [12,18]. Thus, lignin is relegated to low value applications as a source of fuel through combustion and the production of products such as dispersants, emulsifiers, mud-sand cement, floatation agents etc.[19]. However, lignin can be put to better uses following different conversion routes where it is possible to purify it and break it down into small fragments that can be used as platform chemicals in the field of polymers, medicines, cosmetics, adhesives etc. [20]. Therefore, a complete integration of lignin into the bio-based economy requires focussing on the development of processes for lignin transformation high value-added chemical products like phenols.

The conversion of lignin to value added product such as phenols, firstly requires an understanding of the lignin pysico-chemical composition [21]. The properties of native lignins differ depending on the type of lignocellulose, and numerous laboratory and industrial methods are in existence to separate lignin from lignocellulosic materials, and each separation method modifies to some degree the chemical structure of the native lignin. Thus, the reactivity of lignin significantly differ depending on the nature of biomass and the process of lignin extraction [12,22]. Several efforts have been devoted by numerous researchers to develop methods to analyse the chemical

compositions of lignin, which have been reviewed elsewhere [21]. These techniques have provided the knowledge on the lignin chemical structure and possible applications [23]. Despite these efforts, the insight into the lignin characteristics remains an ongoing challenge, with results varying even within similar methods, requiring more efforts in the development of efficient methods to reveal the true identity of lignin [24]. Therefore, the first approach in this project was the development of a new analytical method not well described in literature, and together with other conventional lignin characterisation methods, were used in the identification of the physico-chemical properties of the selected lignins. In this new method [25], lignin was pyrolysed using thermogravimetric analyser (TGA), with the volatiles generated captured in thermal desorption (TD) tubes coupled to the TGA. The TD tubes containing the volatiles were removed from the TGA and characterised for chemical consists using gas chromatography couple to mass spectroscopy (GC-MS). The analytical pyrolysis technique was collectively called TGA-TD-GC-MS. Before the use of this method, the GC/MS was calibrated with standard phenolic compounds. The monomeric chemical products obtained from the lignins and classified into the three primary phenolic compounds commonly found in lignin, as syringol/guaiacol/hydroxyphenyl (S/GH) ratios, could provide reliable information about the biomass origins of the lignins. The analytical method developed had several advantages over other analytical methods which include the use of internal calibration using standard compounds of phenols, known to provide more details of the mass yields of lignin. This is more accurate than peak area quantification methods used by other researchers. It also provide detail information about the mechanistic pathways of the mass loss of sample materials, aside the benefit of small sample size and zero solvent requirements [25,26]. The advantages of handling small sample size and zero

solvent requirement for condensable volatiles treatment before analysis by GC-MS make it beneficial for screening experiments, and hence would provide information for optimisation of processes at larger scale.

With the detail insight into the lignin properties in place, it is well accepted that pyrolysis is a promising and cost effective thermochemical technologies for the depolymerisation of lignin to give various types of aromatic chemicals [27,28]. In pyrolysis technology, biomass is heated in the absence of oxygen to yield char, bio-oil and condensable gases as the major end products [5,29]. With the lignin pyrolysis, the bio-oil produced contains a mixture of monomeric phenols namely, syringol, guaiacol, phenol, 4-vinylguaiacol, creosol, 3-methoxycatechol o-cresol, etc. The distribution of these phenolic products depends strongly on the biomass origin, the methods used to separate them from the lignocelluloses, and the pyrolysis conditions [30]. Therefore, lignin from the hardwood consists of mostly the syringol- and guaiacol-type phenols, softwood lignin predominantly consists of the guaiacol-type phenols, and herbaceous (non-woody) lignin consists of the syringol-, guaiacol-, and hydroxyphenyl-type phenols [30]. In literature, most of the studies have focussed on the pyrolysis of one type or two types of lignins, with emphasis on the kinetics and thermal degradation behaviours of the lignins, with limited information about the phenolic products from such lignins [31–33]. The few that have considered the production of phenols have often compared the phenolic yields based on peak area fractions from GC-MS chromatograms, which do not give accurate estimate of the mass yields of the phenolic products [34,35]. Furthermore, there are limited studies on the production of phenols from the combination of softwood, hardwood, and herbaceous lignins [17]. This is critical for detail optimisation of pyrolysis processes,

which can help with the understanding of the specific process conditions that can maximise the production of phenolic products from the respective types of lignin.

Recent works have shown that chemical products of interest from lignin are generally obtained in a complex mixture and in low yields, where both mass yields and selectivity for phenol products can be improved by the use of catalysts [12]. This is the major objective of this study, which is to investigate the ability of catalyst to selectively increase the yields of phenols during lignin pyrolysis conversion. Most researchers have focused on the production of aromatic hydrocarbons mostly benzene, toluene, and xylene (BTX). The BTX from lignin were obtained using zeolite catalysts as the primary catalysts. BTX have a relatively low market value compared to phenols [19,36]. Phenols have attracted much attention in recent time due to their wide application in the fields of plastic, pharmaceutical, and cosmetic industries [11].

Among the catalysts explored for the production of phenols from lignin, the alkaline and metal oxide catalysts have been reported to be promising due to their availability and low cost [37,38]. The alkaline catalysts include hydroxides and carbonates of the group 1 and 2 elements of the periodic table such as NaOH, KOH, LiOH, $Ca(OH)_2$, K_2CO_3, $CsCO_3$, $RbCO_3$ etc. The metal oxides catalysts include oxides from the group 2, 3 and the transition metal oxides namely Al_2O_3, CaO, Fe_2O_3, TiO_2, ZnO, MgO, CuO, MoO_3, NiO etc. With the alkaline catalysts, the majority have been used to depolymerise lignin to phenolic compounds in solution states [6,39,40]. Although this method has recorded up to 50% improvement in the yield of phenols [41–43], some of the challenges with depolymerisation of lignins in aqueous media are associated with product recovery, high cost of process and use of harsh reaction conditions [13]. With the metal oxides, they have been used by direct mixing of the dry powder with the lignin. However, alternative method such as impregnation, could have a pronounced

effect on the yields of products due to the intimate contact of the catalysts with the lignin, aside the requirement of relatively low (< 10 wt.%) contents of catalyst [44].

Finally, studies to maximise the production of phenols from catalytic pyrolysis of lignin are rare. Most researchers have concentrated on the study of the effects of temperature as a way of optimisation approach [45,46], without the use of catalysts. In this study, the investigated range of temperature and catalyst content were determined at milligram scale, and then applied further at gram scale in a pyrolysis bench-scale reactor.

1.2. Thesis outline

This dissertation consists of **8 chapters**, as presented in the following outlines:

Chapter 2 discusses the different components of lignocellulosic biomass material, with more details on the lignin nature, structure, linkages, and the isolation techniques commonly applied to liberate lignin from other major fractions of lignocellulosic biomass material. It also provides a detailed review of the catalysts explored in the thermochemical conversion of lignin to chemical products, with more emphasis on catalytic pyrolysis of lignin for phenols production.

Chapter 3 presents the research objectives, by providing details as to how the current study has responded to the gaps identified from the review of literature.

Chapter 4 presents the results of the lignin characterisation. Different wet chemical and analytical methods were applied to reveal the physico-chemical properties of the lignins prior to conversion to phenols.

Chapter 5 contains the results of the comparison of the phenols production from the catalytic pyrolysis of lignin from three biomass types namely, hardwood, softwood,

and herbaceous lignins. This was done to establish the yields and selectivity to specific phenolic compounds from the respective lignins.

Chapter 6 presents the results of the screening of various catalysts and lignin types. This was done to establish the most promising catalysts that could be further investigated for optimisation of phenols production.

Chapter 7 presents the results of the investigation into the range of catalysts concentrations from one of the best performed catalysts established in **chapter 6** to identify the best catalyst concentration that maximise the yields and selectivity of phenols from lignin pyrolysis.

Lastly, **chapter 8** outlines the conclusions of the main findings of this study, and some recommendations

1.3. List of publications from the thesis

The thesis resulted in the following publications:

I. Chapter 4:

D.R. Naron, F.-X. Collard, L. Tyhoda, and J.F. Gorgens. Characterisation of lignins from different sources by appropriate analytical methods: Introducing thermogravimetric analysis-thermal desorption-gas chromatography–mass spectroscopy, Ind. Crops Prod. 101 (2017) 61–74.

II. Chapter 5:

Authors: D.R. Naron, F.X. Collard, L. Tyhoda, J.F. Görgens. Title: Influence of impregnated catalyst on the phenols production from pyrolysis of hardwood, softwood, and herbaceous lignins https://doi.org/10.1016/j.indcrop.2019.02.001

III. Chapter 6:

Authors: D.R. Naron, F.-X. Collard, L. Tyhoda, and J.F. Gorgens Production of phenols from pyrolysis of sugarcane bagasse lignin: Catalyst screening using thermogravimetric analysis – Thermal desorption–Gas chromatography–Mass spectroscopy. Journal of Analytical and Applied Pyrolysis. https://doi.org/10.1016/j.jaap.2018.12.015

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CHAPTER TWO

LITERATURE REVIEW

The isolation of lignin from other components of lignocellulosic biomass materials results in severe modification of the lignin native structure, leading to varieties of lignin physico-chemical characteristics depending on the plant source and isolation process. Therefore, a brief review of the different techniques of extraction of lignin from lignocellulosic biomass materials, including the various chemical reaction mechanisms that occur during the isolation processes is presented. Catalytic pyrolysis is the primary focus of this study. Therefore, numerous factors that influence the product distribution during lignin pyrolysis is presented, including the aforementioned properties of isolated lignins. Also reviewed are some of the catalytic depolymerisation strategies that have been developed to selectively control the product distributions from lignin. Emphasis of the review is on the catalytic pyrolysis studies that are relevant to the production of phenol-derived chemical products.

2.1. Lignocellulosic Biomass Compositions

Lignocellulosic biomass is a complex composite that is principally consists of three biopolymers namely hemicelluloses, cellulose and lignin [1]. Both cellulose and hemicellulose polymers combined are referred to as holocelluloses [2], consisting of simple sugars that are largely D-glucose, D-xylose, D-galactose, D-mannose, L-arabinose, D-glucuronic acid, and lower quantities of other sugars such as D-fructose and L-rhamnose. Cellulose is the predominant component of lignocellulose than hemicellulose and lignin, with a range of 30-50% as cellulose, 20-35% as

hemicellulose and 20-35% as lignin [3–5]. Aside the three main components, there are minor amounts of other components namely extractives (which are made up of diverse individual compounds), and ash [4,6,7], with a wide range of chemical structures [8]. Overall, the amounts of the various fractions of biomass depends on the type of lignocellulosic biomass [1].

2.1.1. Cellulose

Cellulose is the most abundant carbohydrate polymer, which make up about 40-60% of lignocellulosic biomass [9]. Structurally, cellulose is a glucan polymer of D-glucose units bound together by β-1,4-glucopyranose units [10,11]. Furthermore, depending on the species of plant, the cellulose structure has a degree of polymerisation (DP) in the order of 600-15000 units, [1,12]. The molecules of cellulose are randomly aligned with great affinity to produce both intra- and intermolecular hydrogen bonds. This orientation, as influenced by these bonds is responsible for the crystalline structure of cellulose, thereby, making cellulose thermally stable [1]. The structure of cellulose also has amorphous regions, which are responsible for its solubility during fractionation [13]. A simplified chemical structure of cellulose is shown in figure 2-1.

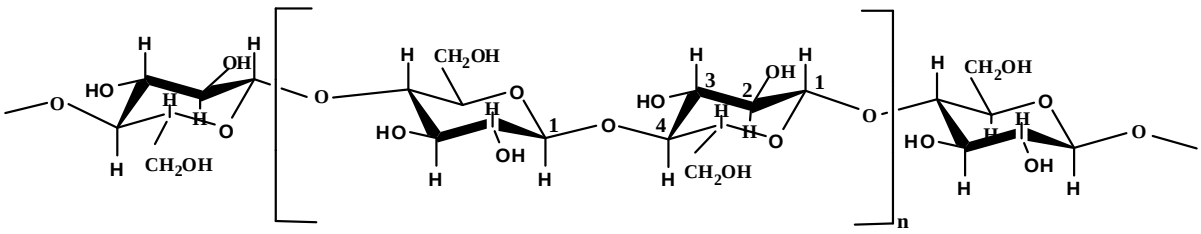

Figure 2-1: Structure of Cellulose redrawn from Jaime Baeza and Juanita Freer[14]

2.1.2. Hemicellulose

Aside cellulose, the other major natural occurring carbohydrate-based polymers are hemicelluloses known to be the second most abundant carbohydrate polymer in nature, making up 20-35% of lignocellulosic biomass [9]. Hemicellulose is structurally composed of C6 and C5 polysaccharides. The C6 polysaccharides are made up of monomeric sugars of hexoses such as D-glucose, D-mannose, and D-galactose, while the C5 polysaccharides are the pentoses such as D-xylose, L-arabinose, and D-arabinose. Hemicelluloses have lower number of sugar units (DP value between 50–300), and more branched structurally than cellulose [15]. Hemicelluloses are built of other minor amounts of sugars such uronic acids (4-O-methyl-D-glucoronic acid, D-galacturonic, and D-glucoronic acid). Depending on the kind of lignocellulosic biomass materials, there are numerous variations among the hemicelluloses components. For example, the principal hemicellulose components in softwoods are galactoglucomannans and arabinoglucuronoxylan. Hardwood hemicelluloses consist of predominantly glucomannan and glucuronoxylan (xylan). In grasses and straw lignocelluloses, xylan is mostly found [10], including 4-O-methyl ether, acetic, p-coumaric, and ferulic acids [14].

2.1.3. Lignin Nature and Structure

Lignin derived its name from the word lignum, meaning wood in Latin [16]. Lignin is the second most abundant biopolymer on earth only exceeded by cellulose [17–19]. Lignin makes up 15-35% of lignocellulose on a dry basis [20]. With over 300 billion metric tonnes availability in varieties of plants on earth, lignin can be regenerated by plants to the tone of 20 billion metric tonnes annually [21]. Global annual production of lignin is within the range of $5 \times 10^8 - 3 \times 10^{11}$ tonnes [21–24]. Lignin interlinks

hemicellulose and cellulose, and give structural support to fibrous lignocellulosic plants [25], and is the part that is responsible for the structural rigidity of lignocellulosic biomass against mechanical stress [20,26]. Furthermore, lignin provides protection against fungi and bacteria to the polysaccharides [27]. The amount of lignin varies from plant to plant [10], and varies by mass within the range of 20-30% [28]. The physical and chemical constituents of lignin can vary depending upon the lignocellulosic plant species [29], the environment from which the wood is harvested, and the process by which the lignin is isolated [4,30]. Lignin has a complex chemical structure [31], and is described as an amorphous polyaromatic cross-linked macromolecule, produced by enzymatic polymerisation of three types of phenylpropanoid monomers called p-coumaryl (H), coniferyl alcohol, and sinapyl alcohol (S) units [20,32–35]. The designation phenylpropanoid monomers are based on their aromatic (C_6) ring and propane (C_3) pattern [36]. The nomenclature of the monomers starts with the substituent carbon as C_1, while the phenyl (aromatic) carbon attached to the hydroxyl (-OH) groups as C_4 [36]. The methoxy (-OCH_3) groups (s) in the monomeric structures are numbered such that they fall on lower carbon atom (C_3) depending on the direction of numbering. The propane subunits are labelled as alpha, beta, and gamma (α, β, and γ). Replacement of the aromatic ring with one methoxy group (CH_3O-) on position 3 or 5 as exemplified by Figure 2-3 gives guaiacyl, also known as coniferyl alcohol. The occupation of methoxy groups (CH_3O-) on both position 3 and 5 of the aromatic ring gives syringyl units also known as sinapyl alcohol while substitution of the aromatic ring with hydrogen atom on both positions 3 and 5 gives p-coumaryl alcohol unit also called p-hydroxyphenyl unit. The guaiacyl lignin is dominant in the softwoods, while a mixture of sinapyl and guaiacyl monomers are found in the hardwoods [37]. Straw and grasses comprise of guaiacyl,

syringyl and p-coumaryl structural monomers. In general, the lignin content in grasses are less than those of softwood lignins [32,38]. The different monomer units of lignin are presented in Figure 2-2.

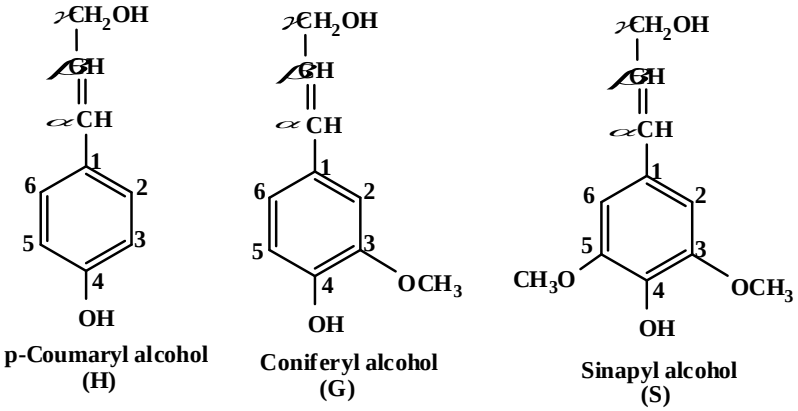

Figure 2-2: The three building blocks of lignin redrawn from Kang et al. [39]**.**

The coupling of these three different monomers by polymerization results in the formation of a highly branched lignin structure linked by different types of bonds, namely aryl ether bonds (β-O-4 and α-O-4), diphenyl ether (4-O-5), carbon-carbon bonds such as diphenyl methane (β-1), pinoresinol (β–β), phenylcoumaran (β-5), and biphenyl (5–5) [40,41]. The β-O-4 ether bond is the most frequent linkages [20,42], representing up to 60% of the total inter-unit linkages in lignin [43]. Table 2-1 shows examples of common monomer linkages found in lignin from softwood (SWD) and hardwood (HWD). Figure 2-3 demonstrates the structural linkages between the monomers of lignin, leading to the formation of lignin polymers.

Table 2-1: Linkages found in softwood and hardwood lignin

Linkage Type	Dimer Structure	% Linkages in SWD	% Linkage in HWD
β-O-4	Arylglycerol β-aryl ether	45-50	60
5-5	Biphenyl and Dibenzodioxocin	18-25	20-25
β -5	Phenylcoumaran	9-12	6
β -1	1,2-Diaryl propane	7-10	7
α-O-4	Phenylpropane α-aryl ether	6-8	7
4-O-5	Diaryl ether	4-8	7
β - β	β-β-linked structure	3	3

Source: Adapted from Ricardo et al. [44].

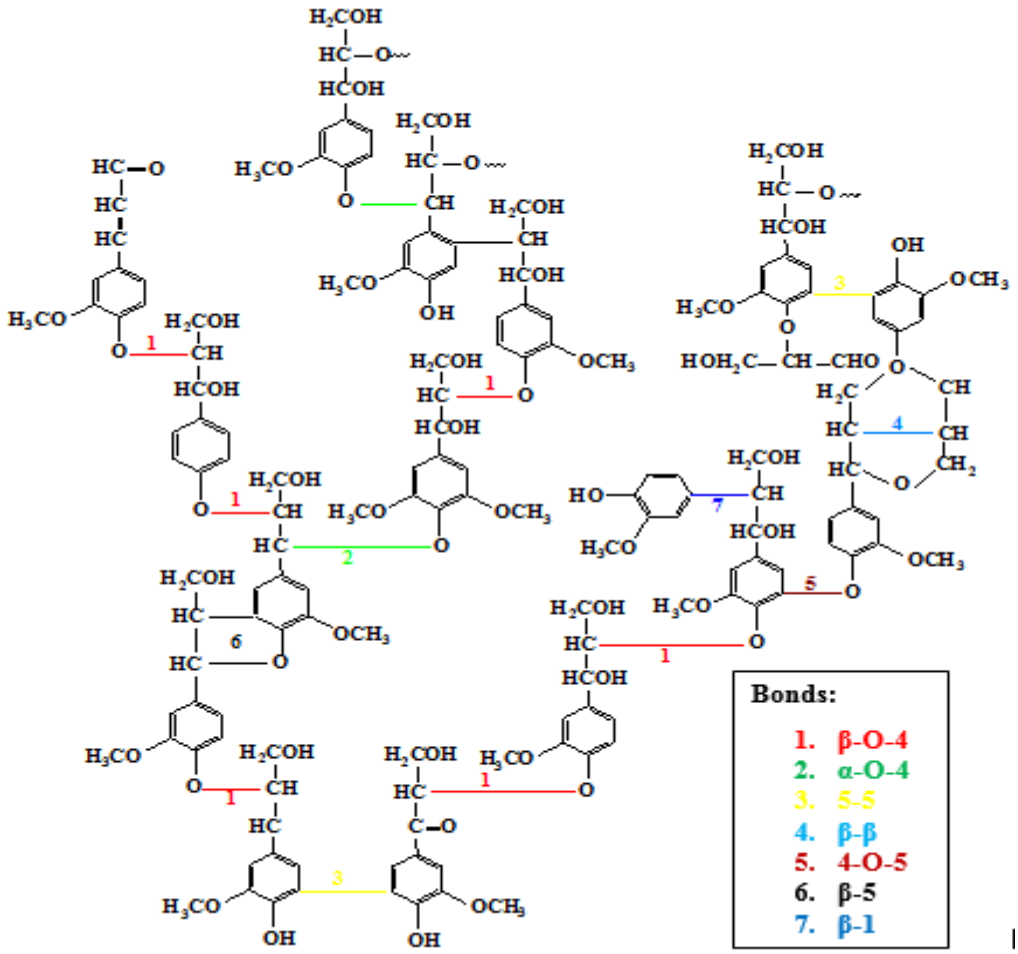

Figure 2-3: Different linkages in softwood lignin redrawn from Laurichesse & Avérous [45].

Aside from these linkages, lignin also has several functional groups on the building block units. The most common ones are the methoxy group (CH_3O-), aliphatic hydroxyl group (-OH), phenolic hydroxyl group (Ph-OH), carboxyl group (-COOH), and trace amount of the ketone and aldehyde-type carbonyl groups (-C=O). The amount of these functional groups depends on the degree of purity, molecular weight, as well as the isolation method. The various linkages and functional groups associated with lignin give lignin a unique and complicated heterogeneous structure (Figure 2-4). Although the most important structural features of lignin are fairly well understood after many years of studies, the uncertainty to the true chemical structure of lignin still

remains unresolved [36]. Figure 2-3 is also a typical structure of lignin resulting from the coupling of the three monomeric C_9 lignin units. Furthermore, as plants age, lignin composition vary within the same plant [46,47]. These differences in the concentrations of lignin results in variation in the chemistry of lignin within the same plants and between plants [36]. Furthermore, the linkages and the functional groups present in lignin behave differently during depolymerisation due to differences in bond energies.

2.1.4. Extractives and Ash

Beside holocelluloses (hemicellulose and cellulose) and lignin, there are other diverse natural products known as extractives present in lesser amounts, generally between 2-10% depending on the plant source [12]. They are called extractives because they are commonly isolated from lignocelluloses using water as solvent or organic solvents like acetone, hexane ethanol, toluene benzene, etc. Examples of extractives include starch, pectin, turpenoid compounds, phenols, ash, resin acids, fatty acids, waxes, alcohols etc [1]. The chemical constituents of extractives exist as monomers, dimers, and polymers whose concentrations differ depending on the type of lignocellulose [12]. Some of the extractives present in lignocellulosic biomass materials are responsible for their characteristic smells and colours, as well as their longevity [48].

Aside the extractives, there are mineral salts or inorganic matter present in lignocellulosic biomass materials. The concentration of the inorganic constituents varies widely in and among plant species depending on the environment of growth of the plant [12]. These inorganic contents are collectively referred to as ash, considered to be the residue remaining after the lignocellulosic biomass material is incineration at a temperature of 575 ± 25^{o}C [12]. When analysed for contents, the ash consists of

different oxides of several elements such as SiO_2, Na_2O, Fe_2O_3, PbO_2, TiO_2, K_2O, CaO, MgO, MnO_2, ZnO, P_2O_5, NiO, CuO, Al_2O_3, etc. [49]. The ash present in lignocellulosic plants can vary greatly between plant species, depending on their stages of growth, the time of year, and their location [12]. The inorganic minerals inherent in lignocellulosic biomass as ash have great influence on the product distribution of biomass during pyrolysis [1].

2.2. Lignin Sources, Isolation Methods and Compositions

Lignin is problematic for the pulp and paper industry and inhibits the use of cellulose to produce biofuels [44,50]. In the paper and pulp industry, the process involves the use of pulping chemicals known as white liquor to selectively solubilise lignin by degradation and/or derivatisation, thereby, freeing cellulose fibres for the production of paper and other products [15]. The biological substances like lignin, hemicellulose, and a small fraction of the cellulose, dissolve in the cooking liquor. These organic materials together with the inorganic portion of the cooking liquor are collectively referred to as black liquor or spent liquor [15]. The physico-chemical characteristics of the spent liquor depend on the feedstock, pulping conditions, equipment, and the treatment applied [15]. The spent liquors are mostly generated from the pulping of hard and soft woods. More recently, interest has been extended to the pulping of non-woody lignocelluloses such as bagasse, straw etc. Generally, the constituents of spent liquor include water, lignin, polysaccharides, carboxylic acids, extractives, and pulping chemical such as NaOH, Na_2S, Na_2CO_3, Na_2SO_4 etc. [51]. The pulping of non-woody lignocelluloses generates spent liquors that contains considerable amounts of aluminium and silica [15]. As a routine process in the pulping mills, the organic fraction of the spent liquors is recovered for use as complementary source of heat and electricity in recovery boilers. Alternatively, the solubilised lignin, which is one of the

main constituents of the spent liquors can be extracted by acid precipitation as a chemically modified forms of natural lignin [52], for use in value-added applications. The inorganic portion of the spent liquor can be recovered in a form that can be use again in the pulping process.

In the bioethanol production from lignocellulosic biomass materials, several conversion steps are involved, with the main stages involving pre-treatment, enzymatic hydrolysis of fermentable sugars and hemicellulose, and fermentation [4]. The objective of the pre-treatment stage is to rupture the lignin structures, and disrupt the cellulose crystalline structures [4], rendering the lignocellulosic material amenable to hydrolysis and fermentations. The lignin residue recovered from these processes can be utilise in value added application. Beside these two industrial sources of lignin, over 300 billion tonnes of lignin are in existence in the biosphere with a yearly increase of approximately 20 billion tonnes [53]. Despite these huge amounts, majority of the lignins end up as sources of fuel via combustion with minimal amounts ($\leq$ 2%) being utilised in value-added applications [54].

The techniques available to isolate lignin restructure the natural lignin (protolignin) to some extent, and the lignin is named according to both the type of lignocellulose and the techniques of isolation [53,55]. A number of lignin isolation methods are presently applied in research and industry and can be divided into two, as industrial and analytical separation methods. industrial lignins are obtained from the Kraft (sulphate) pulping, sulphite pulping, sulphur-free alkali (soda) pulping, organosolv pulping, and steam explosion combined with enzymatic hydrolysis. The analytical lignins include acidolysis lignin, milled wood lignin (MWL), enzymatic mild acidolysis lignin (EMAL), hydrolytic lignin and Klason lignin [55,56]. This study focused on industrial lignins coming from the Kraft, sulphite, soda, soda-anthraquinone pulping processes

as well as steam explosion combined with enzymatic hydrolysis, and are discussed thus:

2.2.1. Kraft process lignin

The foremost pulping process is the Kraft or sulphate pulping [20]. The reasons for the dominance are related to wood quality, short cooking times, and well-established recovery of cooking chemicals, energy, and by-products [15]. The technique encompasses the use of aqueous sodium sulphide (NaS_2) and sodium hydroxide (NaOH) under alkaline conditions to isolate the cellulosic component through a digestion process that dissolves lignin and most of the hemicellulose present in the lignocellulosic biomass. After digestion, the spent liquor is separated from the pulp by washing, and then concentrated to a solid content within the range of 65-80% using multiple-effect evaporators. Finally, the pulping chemicals used during the process are recovered by incineration in the recovery furnace, which also generates steam and electricity for the process from the lignin rich-black liquor.

During Kraft pulping, lignin goes through serious fragmentation and condensation reactions, leading to significant structural and chemical changes compared to the natural lignin. For example, the carbon-carbon linkages connecting the phenylpropane units are more in number than that of the native biomass [20]. The presence of ionic species namely, hydrogen sulphide (HS^-) and hydroxyl (OH^-) ions in the cooking liquor caused severe degradation of the lignin, leading to the generation of phenolate and carboxylate ions [57]. Fragmentation of the inter-units of cellulose and hemicelluloses also occur significantly. Hemicelluloses are converted to hydroxycaboxylic acids and a trace of dissolved polysaccharides are found in the final spent liquor due to incomplete degradation [57]. A complex mixture consisting of

small molecular mass phenolic products (monomer derived) and giant molecules are produced due to dissolution and degradation of lignin [15]. Many of the fragments from the lignin (in the form of sodium phenolates) in the white liquor are water soluble. With the right reaction conditions, the lignin fragments forms new C-C bonds (condensation), which can results lignin fractions with high molecular mass [15]. The essential reactions that occurs during Kraft pulping are the cleavage of several bond linkages such as α-O-4 and β-O-4 bonds, etherified and non-etherified phenolic bonds, demethylation and condensation reactions [15,51]. Overall, the reactions that happened during Kraft pulping are complicated and therefore, the mechanistic pathways that lead to lignin modification remains a challenge. The lignin resulting from Kraft pulping has a chemically bound sulphur, which limits its utilisation in value-added application, leading to recent interest in sulphur-free lignins [6]. Furthermore, the Kraft process is associated with poisonous gases and bad odour due to the presence of organic sulphides such as aliphatic thiols, which cause environmental concern [57,58]. Meanwhile, Kraft pulping versatility to handle diverse types of woods gives it an edge over other pulping processes [15,57]. The depolymerisation mechanism of lignin during Kraft pulping is shown in Figure 2-4.

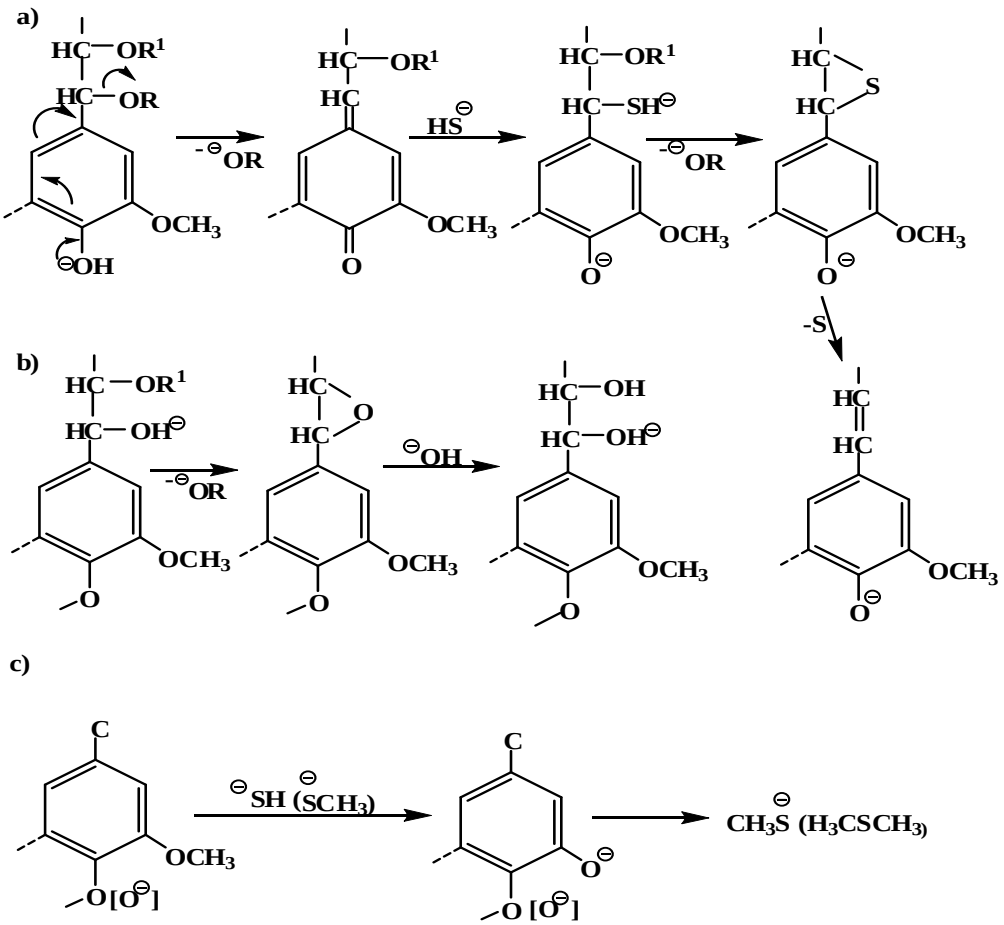

Figure 2-4: Lignin degradation reactions during Kraft Pulping Redrawn from Allen [15]**.**

2.2.2. Sulphite process lignin

This pulping method has been in use for more than 130 years before its dominance ended around the 1940s [59]. Today, the sulphite pulping makes up just about 10% of the global pulping processes with ≤ 1 million tonnes of pulp per year [60]. The sulphite process uses a solution of sulphur dioxide known as sulphurous acid (H_2SO_3) and bisulphite (HSO_3^-) of ionic calcium, magnesium or sodium [20], and is performed at acidic or near- neutral conditions. Therefore, SO_2 (sulphur dioxide), HSO_3^- (hydrogen sulphite ions), and SO_3^- (sulphite ions) are the active species present during sulphite process. The amounts of these sulphur-related species depend on the pH of the digestion liquor [15]. Three major reactions steps occur during sulphite pulping to

separate lignin namely sulphonation, hydrolysis, and condensation. Delignification is achieved through the combined effects of sulphonation by HSO_3^- ion and hydrolysis reactions steps. The sulphonation reaction acts to soften the lignin and makes it more hydrophilic. The hydrolysis breaks the lignin aryl ether bonds so that new and smaller soluble lignin fragments are formed [15,57]. In this condition, the lignin becomes highly soluble in water due to the incorporation of the sulphonic acid groups into the alpha-carbon atom of the phenylpropane structure in place of the hydroxyl or etherified groups [15].

Compared to the Kraft lignin, sulphite lignin contains more sulphur, and exhibits higher molecular weights, which is ascribed to the creation of sulphonate functional groups on the lignin build [54]. There are several modifications of the sulphite process in place in recent time to improve both reaction kinetics and pulp yields. They include acid sulphite, bisulphite, neutral sulphite semi-chemical (NSSC), and anthraquinone (AQ) alkaline sulphite. The AQ alkaline sulphite pulping is used to giving it a Kraft-type pulps. Table 2-2 shows the various modified sulphite processes commonly applied in the pulping industry. The chemistry surrounding lignin breakdown during sulphite and NSSC is restricted to phenolic lignin units involving alpha-hydroxyl or alpha-ether bonds cleavage. The low molecular weight compounds formed during both processes are namely aldehydes (vanillin and syringaldehyde), acids (vanillic, syringic and hydroxybenzoic acids), ketones (acetovanillone and acetosyringone), and alcohols (syringol and dihydroconiferyl alcohol) [15]. Sometimes, sulphite lignin is referred to as “lignosulphonate”, meaning the neutralised lignin units liquefied in the cooking liquor [15]. The introduction of AQ as catalyst accelerates the delignification dramatically and stabilises wood carbohydrates in the pulping process. AQ enhances delignification by promoting the cleavage of free-phenolic beta-aryl ether linkages

[61]. Hardwood, scientifically called *Eucalyptus grandis* (*E.Grandis*), and a mixture of *E. Grandis* and pine (softwood) are the primary feedstock. The lignin reactions that occur during sulphite pulping is shown in Figure 2-5.

Table 2-2: Sulphite Pulping Processes Adapted from Allen [15]**.**

Process	**pH**	**Base**	**Active reagent**	**Pulp type**
Acid Sulphite	1-2	Na^+, Mg_2^+, Ca_2^+, H_4N^+	HSO_3^-, H^+	Dissolving pulp Chemical pulp
Bisulphite	2-6	Na^+, Mg_2^+, H_4N^+	HSO_3^-, H^+	Chemical pulp High-yield pulp
Neutral Sulphite (NSSC)	6-9	Na^+, H_4N^+	HSO_3^-, SO_3^{2-}	High-yield pulp
AQ Alkaline	9-13	Na^+	SO_3^{2-}, HQ^-	Chemical pulp

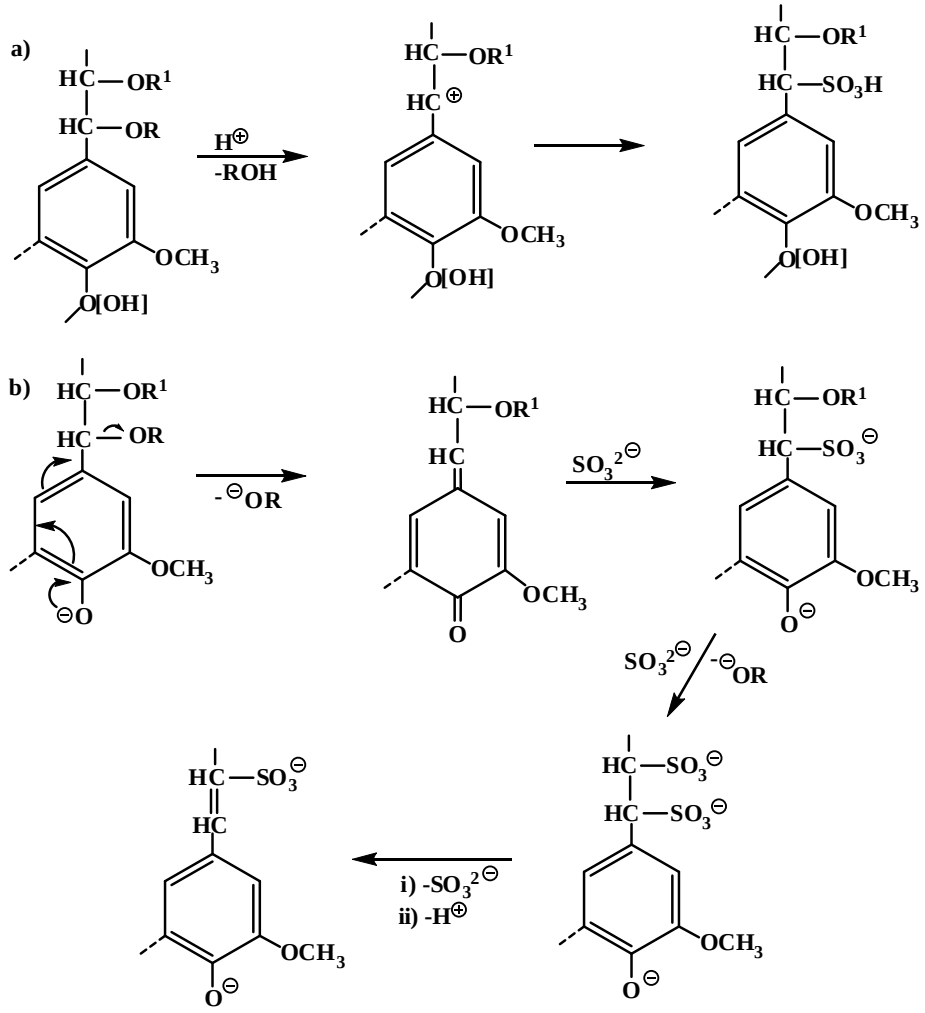

Figure 2-5: Reactions of lignin in acid sulphite and bisulphite pulping (a) and neutral sulphite and alkali sulphite pulping (b). R is H or aryl group, R^1 is aryl group. Redrawn from Allen [15]

2.2.3. Soda and soda-anthraquinone process lignin

Soda pulping or sulphur-free alkali pulping, makes up around 5% of the global pulp manufacture, and is good for the pulping of non-woody lignocelluloses such sugarcane bagasse and grasses [20]. Unlike the Kraft pulping which uses NaOH and Na_2S as pulping chemicals, the Soda pulping uses NaOH as the only active chemical. To produce a pulp (cellulose) of sufficient purity, the requirement for delignification

is about 10-15% NaOH based on raw material. The lignin removal reactions involve the scission of α-, β-linkages [62]. Meanwhile, chemical action and solubilisation make sodium ions, carboxyl and phenolic hydroxyl groups of lignin bond chemically, producing carboxylate sodium and phenolic sodium groups. In some cases, as with sulphite lignin, additive such as anthraquinone (AQ) derivatives are added to stabilise carbohydrates and dissolve lignin, thereby increasing the yield [63]. The addition of AQ to alkaline pulping process is also to increase lignin separation by enhancing additional breakage of intermediate linkages in lignin fragments [61]. The general mechanism for the reaction of AQ with the soda pulp components involved electron transfer by oxidation of aldehyde terminal groups to alkali-stable aldonic acids with a simultaneous formation of anthrahydroquinone (AHQ). The AHQ is converted back into AQ by reacting with the lignin material, due to the cleavage of β-aryl ether linkages, and this reaction accelerates the rate of delignification [15]. AQ also helps minimise re-condensation reactions via reactions with carbohydrates, leading to increased removal of lignin during pulping process [64]. The lack of Sulphur in the Soda-AQ process makes it promising for the advancement of biorefinery, as lignin devoid of Sulphur is produced, which could be utilised in the production of fuels and chemicals.

2.2.4. Steam explosion process lignin

The steam explosion process is a modification of the autohydrolysis conditions, which is basically a steam hydrolysis process conducted at elevated temperature [65]. Steam explosion process lignin is obtained based on the pre-treatment of lignocellulosic biomass material with elevated pressure steam, and then rapidly depressurised [4,47]. These actions structurally modified the lignin and deconstruct the crystalline structures of the cellulose and hemicellulose. The presence of some organic acids

released during the process caused the hydroxyl groups on the alpha carbons of the lignin structure to become reactive, leading to the generation of carbonium ions [54,66]. This triggers two competing reactions, which are destabilisation of the β-O-4 bonds that exist between the phenolic groups, and depolymerisation of the lignin monomers [23,67]. In steam explosion pre-treatment technique, as with some other pre-treatment methods, lignin is concentrated in the solid fraction of the pre-treated material [68]. The pattern of lignin degradation during steam explosion pre-treatment is shown in Figure 2-6. Depolymerisation of lignin produces phenolic hydroxyl groups (A) and quinones (B). The breakage of the β-O-4 bonds (C) generates radical species that can undergo further reactions such as re-polymerization therefore, forming different types of chemical products such as oligolignols, phenols and carboxylic acids [38].

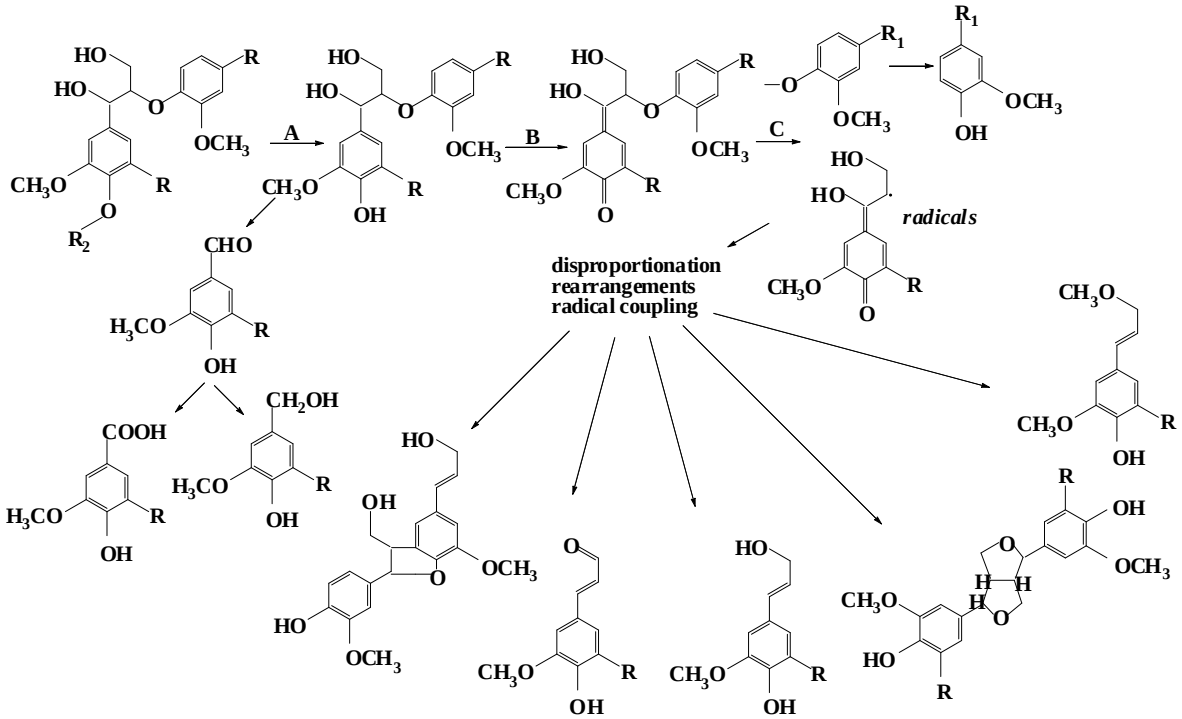

Figure 2-6: Pattern of lignin degradation during steam explosion pre-treatment redrawn from Luiz [38]**.**

The lignin obtained from steam explosion pre-treatment usually has an average molecular mass of about 2000, rich in phenols because of hydrolytic processes [69]. The removal of hemicelluloses during steam explosion pre-treatment exposes cellulose by increasing its surface area making it more amenable to degradation by enzyme. On application of cellulase and hemicellulase enzymes, most of the remaining carbohydrates in pre-treated solid are hydrolysed and thus removed, resulting in lignin-rich residue with a purity in the range of 80-97% [70,71]. Steam explosion lignin has similarities with organosolv lignin (known to have low structure degradation) and resembles native lignin based on properties and molecular weight [47,58]. The phenolic oligomers from the steam explosion lignin contain 3-12 benzene rings per oligomer unit [47]. As with the soda-anthraquinone lignin, the absence of sulphur makes it promising to produce phenolic chemicals.

2.3. Conversion of Lignin to chemical products

The valorisation of lignin is critical to the current utilisation of biomass to produce high value products such as short chain molecules, bio-polymer materials, and fuels whose sources come mostly from the petrochemical industries [72].

For decades, while research have established routes for chemical and fuel productions from cellulose and hemicelluloses portions of lignocellulose, to platform chemicals, there is currently inadequate technologies that can convert lignin, despites its being the greatest relevant replenishing source of aromatic chemicals on earth [18]. The complexity surrounding the lignin chemical structure limits its application to fuel for heat and electricity, to augment the energy needs of the same processes that led to its separation from lignocellulose. However, the burning of lignin can results in the formation of hazardous chemicals such as polycyclic aromatic hydrocarbons (PAHs)

and its oxygenated derivatives, dioxins, particulate matter etc, due to incomplete combustion, and therefore, could have serious effect on the environment [73]. Alternatively, lignin has been utilised in the production of dispersants, binders, emulsifiers, water treatment, oil drilling, carbon fibres, polyurethanes etc., which can be of low quality due to the presence of impurities from improper delignification, and the limitations of the current technologies that produced them [54,58,73,74]. Aside these mentioned applications, lignin can offer significant higher value-added opportunities to enhance the operation of a lignocellulosic bio-refinery; by conversion to low molecular weight chemical products [75–77]. The potential chemical products of high market value that can be obtained from lignin are shown in Figure 2-7.

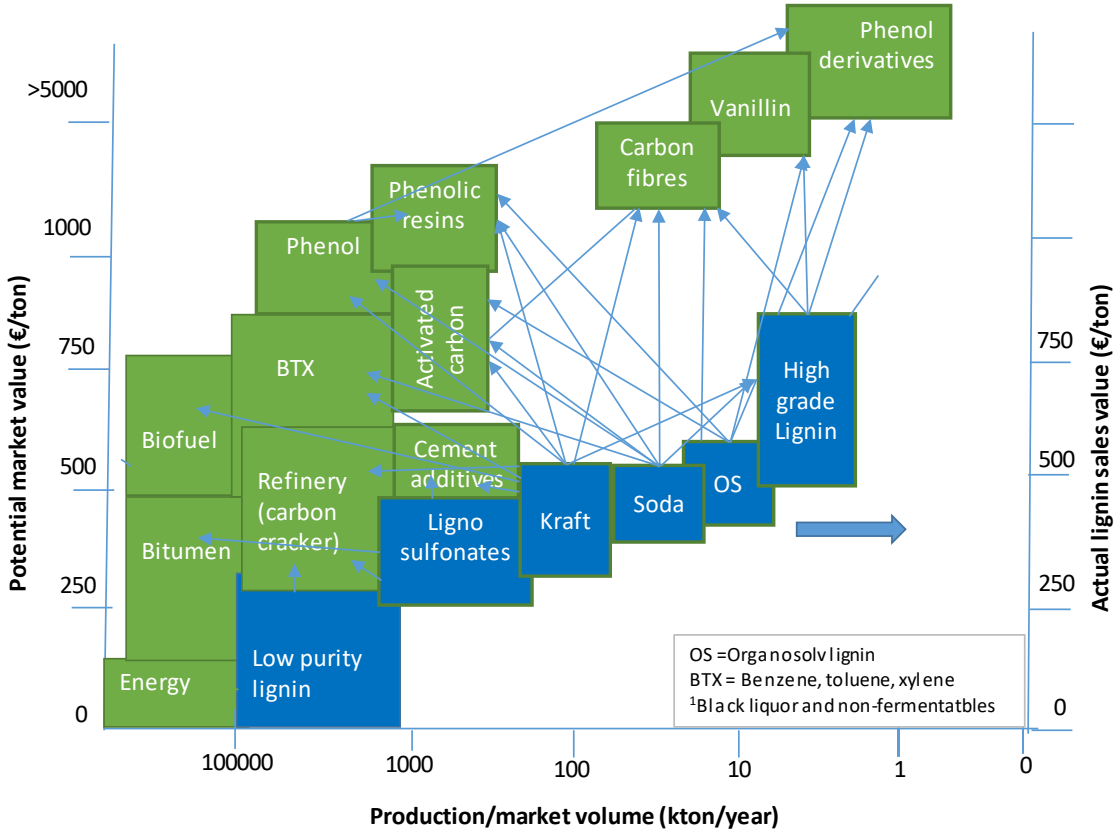

Figure 2-7: Chemical products from Lignin based on Market Value. Redrawn from Wild and Huijgen [78]**.**

Based on Figure 2-8, the potential chemical products of high market value are phenol derivatives such as guaiacol, phenol, catechol, creosol, syringol, eugenol, vinylguaiacol, etc. These chemical products are collectively referred to as phenols. Phenols are platform chemicals utilized in the production of medicines, foods, cosmetics, pesticides, binders and fuel [79]. The volume of phenols produced annually worldwide is up to 8 million tonnes [79]. 1 tonne of phenols is about USD1500 in the market [80], and has continuously increased [81].

Numerous pathways are available for transformation of lignin by depolymerisation to chemical products. Some employed liquefaction technologies like base-catalysed, acid-catalysed, metallic-catalysed depolymerisation means. Also, ionic liquid-assisted

and supercritical fluid-assisted means of lignin transformation have been sorted [82]. However, low yield and non-selectivity of products are the major drawback. This is due to difficulty in the breakage of bonds between lignin monomeric units [83].

In recent time, biocatalytic processes are being developed through the use of enzymes to establish routes of lignin depolymerisation to chemical products [25,84]. Also, of recent is the use of a technique known as reductive catalytic fractionation (RCF) [85–87]. This technique is a combination of lignin isolation and depolymerisation [87]. The process is done in company of reduction catalysts like Ru, Ni, Pb, or Pt using hydrogen gas or hydrogen donating agents, leading to the formation of stable intermediates [86]. This approach has yielded high yields of phenolic products, up to ≥ 50% increase [85]. However, the RCF method is complicated, and faced several challenges related to catalyst and product recoveries, contamination of products, used of hash reaction conditions like the use of hydrogen gas, high pressure (40-60 bar), and long resident time. Table 2-3 shows some of the various yields of monomeric chemical products obtained from these methods of depolymerisation.

Table 2-3: Various depolymerisation methods that obtained chemical products from lignin

Depolymerisation Method	Catalyst/ Solution	Reaction Temperature ranges (ºC)	Major Products	Yield ranges (wt. %)
Based Catalysed Liquefaction	NaOH, KOH, K_2CO_3, $Ca(OH)_2$, LiOH	270-330	Guaiacol	0.9-2.8
			Catechols	0.8-4.9
			Vanillin	0.3-0.5
			Syringols	4.1
Acid Catalysed liquefaction	Formic acid/ethanol	360-380	Phenols	0.3-2.0
			Catechols	0.5-1.7
Metallic Catalysed Liquefaction	Si-Al, ZrO_2-Al_2O_3-FeOx, Ni/C, NiLa/C, NiLa/C, NiPt/C, NiCu/C, NiPd/C, and NiCe/C	200-350	Phenols	0.13-6.5
			Guaiacol	0.06-12
			Catechols	1.3-4.9
			Syringols	36
Ionic Liquid-assisted Depolymerisation	[EMIM][CF_3SO_3]/$Mn(NO_3)_2$, [EMIM][Ace]	100-150	Guaiacol	7.9-75
Supercritical Fluids-assisted Depolymerisation	Water/ CO_2/acetone, methanol/KOH, ethanol/KOH,	290-420	Phenols	1.6-7.53
			Guaiacol	1.6
			Catechols	28.37
			Syringols	3.6
			Cresols	11.67
Enzymatic depolymerisation	Bacterial consortium	30ºC, 15 days	Unspecified monomers	60% (monomers)
Reductive catalyst Fractionation	Ru/C	Methanol, 225 ºC/H_2	Guaiacols syringols	54 wt.%
Reductive catalyst Fractionation	Ni/C	Methanol, 225 ºC/H_2	Guaiacols syringols	68 wt.%

Source: Adapted from Wang et al., Xu et al., Sun and Barta [25,82,87]**.**

From Table 2-3, it can be observed that phenolic chemical products have been produced from lignin conversion catalyzed by relatively cheap (metal carbonate and hydroxides, combined with some solvents) and expensive catalysts (transition metals supported on carbon and ionic liquids). The yields of the chemical products obtained by liquefaction are low despite the use of catalysts, and further improvement is

required. A high value chemical product (guaiacol) has been produced using ionic liquids. Ionic liquids are technically attractive but they are expensive and therefore, not economically attractive at this stage [25]. The use of catalysts in combination with diverse types of supercritical fluids have been shown to produce high value-added chemical products. However, the limitations of these methods include extreme operating conditions and difficulties with product recovery [25,73,88].

In recent past, pyrolysis has been revealed as one of the most favourable technologies to transform lignin to chemical products since pyrolysis is relatively inexpensive in terms of cost, utilises less extreme process/reaction conditions; and produces a more even distribution of chemical products than other technologies such as liquefaction [89,90]. Therefore, a study of the potential of pyrolysis to produce chemical products and the influence of catalysts appears as worthwhile.

2.4. Pyrolysis of Lignin to Chemical Products

Pyrolysis entails heating a biomass in an oxygen-free environment with or without catalysts, resulting in char, gases, and bio-oil as the primary products [35,91]. In pyrolysis, molecules breakdown by heat, starting at the specific points in the structures that have the lowest bonding energies [91]. There are two stages of reactions that occur during pyrolysis namely primary and secondary reactions. The primary reactions imply direct thermal decomposition of the biomass material to vapours and leads to the formation of volatiles and are known as depolymerisation and fragmentation [92]. Secondary reactions are the reactions resulting in the splitting of lignin substituents and repolymerisations of the vapours generated in the primary pyrolysis reactions stage. Bio-oil is an admixture of several hundreds of compounds produced by primary and secondary reactions [93]. For lignin pyrolysis, bio-oil is

composed of monomeric phenols and high molecular mass phenols comprising of 2-5 monomers. The difficult nature and low volatility of the oligomers due to a high molecular mass have limited their detection and characterisation by GC-MS [94,95]. Report from Mu et al. [96] indicated that nearly 40% of the bio-oil originating from lignin cannot be identified using the GC and hence, alternative methods like the FTIR, GPC, and NMR have been employed. In the case of derived monomers, literature studies on GC-MS analysis of lignin-derived bio-oil reported the yields of the chemical products generated from lignin in terms of surface areas of peaks in these chromatograms. Such outcomes are incomparable as surface area of the chemical products does not represent the actual mass yields, but a crude estimate of product selectivity.

Based on the complexity of the chemistry of lignin pyrolysis, it seems that phenols manufacture from lignin can be optimise using some strategic approaches. The commonest monomeric phenols detected in lignin-derived bio-oils include guaiacol, alkylguaiacol, syringol, syringaldehyde, vanillin, vanillic acid, cresol, phenol, catechol, alkyl phenol, eugenol, etc. The amounts of these monomeric phenols vary substantially, and few papers have focussed on the maximisation of monomeric phenols yields. The main parameters influencing the bio-oil yield and composition from lignin pyrolysis are reaction temperature, heating rate, residence time, and type of feedstock [93,97,98]. By understanding the influences of the main factors on the lignin pyrolysis process, the pyrolytic conditions can be predicted and better controlled to limit unwanted side reactions and promote the production of the products of interest (monomeric phenols). Because the phenols yield is lower than in competing process technologies like RCF, catalytic options should be researched to improve both yields and selectivity [88].

There are a number of pyrolysis studies that have been conducted using variety of analytical methods at milligram scale, using TGA connected with on stream analysis of the generated volatiles using FTIR or MS [72,99] and at bench scale using GC-MS to evaluate the generated bio-oil [89,100–102]. Whereas TGA studies are advantageous to study pyrolysis pathways and the impact of reaction temperature on the stable nature of the numerous functional groups, studies at bench scale (larger pyrolysis reactor) provides more insight into the quantities and makeups of the products generated.

2.4.1. Effect of Lignin types on pyrolysis chemical products

Lignin has different chemical structures as a result of diverse origins and different isolation methods [103]. Hence, the bio-oil from pyrolysis processes will have some significant differences in the product distributions. Therefore, it is important to discuss the distributions of the chemical products based on both biomass type and the isolation methods.

As discussed in section 2.1.3, the origin of lignin is known by the relative abundance of p-hydroxylphenyl (H), guaiacyl (G), and syringyl (S) units. Therefore, bio-oil from the pyrolysis in mild conditions of the G type such as softwood lignin mainly yields phenols that are predominantly guaiacol and its derivatives (guaiacol, alkylguaiacol, vanillin, vanillic acid, phenol, alkylphenol, etc.) [104]. Pyrolysis of syringyl-guaiacyl (S/G) type lignin such as hardwood produced syringol and its derivatives (syringol, syringaldehyde, methoxysyringol, allylsyringol etc.), as well as guaiacol and its derivatives [99]. Non-woody plant lignins contain similar proportions of G, S, and H (G/S/H) units [105]. Therefore, the chemical products make-up of the bio-oil from non-woody plants consists of mixture of phenols from G/S/H units in almost similar

proportions. These variations in the chemical products based on lignin types from lignin pyrolysis have different degrees of methoxylation with hardwood chemical products having more methoxy groups in its chemical products than softwood and non-woody chemical products on the main lignin building units [106]. As reported in section 2.4.3, in severe conditions, the methoxy substituent become unstable and can be substituted by methyl or hydroxyl groups, leading to the formation of additional products [92].

In terms of isolation methods, section 2.2 has described the various isolation methods to obtained lignin. The degree of depolymerisation of lignin during the isolation processes differs, resulting in lignins with different molecular weights [106]. The lignins consist of different chemical functional groups such as hydroxyl, methoxy, but also some other functional groups such as sulphur-related functional groups introduced during the isolation processes [106]. The formation of new chemical functional groups during the isolation process will influence the product distribution. Moreover, inorganic materials introduced during isolation processes as additives have a catalytic effect which could influence the pyrolytic process conversion leading to a bio-oil [92].

A number of lignins from different plant species and isolation methods have been investigated. Brodin et al. [107] investigated two Kraft lignins of softwood and hardwood (*E-globulus* and birch trees, respectively) Kraft lignins by prolysis. They observed that the evolution of the chemical products from the two plants species occurred at different temperatures. They obtained phenols around the temperature of 400^{o}C from hardwood while phenols where obtained between 500-600^{o}C in softwood. The stability of the guaiacyl units due to their condensed structure is responsible for the higher range of temperature exhibition during thermal treatment. Li et al. [108]

fast-pyrolysed two softwood Kraft lignins and obtained mostly guaiacol derivatives, with guaiacol, 4-methylguaiacol, 4-vinylguaiacol, and vanillin as the major compounds. The Kraft lignins studied were found to compose of guaiacol-type units (G-type lignin). Ben & Ragauskas [109] also obtained mostly G-type phenols when they pyrolysed softwood Kraft lignin. Yang et al. [111] obtained G-, S-, and H-phenols wheat straw EMAL lignin by employing fast pyrolysis means. Similarly, Trinh et al. [102] fast-pyrolyed wheat straw lignin obtained from ethanol manufacture, and obtained guaiacol, syringols, and 4-vinylguaiacol among the generated compounds. Jiang et al. [101] pyrolysed mixed hardwoods lignin (from un-specified biomass) isolated by the organosolv process, and mixed non-woody lignin (wheat straw and Sarkanda grass) isolated by soda process. The composition of the pyrolysis phenolic products included guaiacols, syringols and phenols derivatives for both lignin mixtures.

Based on these literatures, a conclusion can be drawn that the type of plant where the lignin originates, is an important characteristic that influenced the type of chemical products from lignin pyrolysis. Although many studies on the influence of the isolation methods on product composition have been reported, the one concerning steam explosion sugarcane lignin pyrolysis is rare. Instead, pyrolysis of steam explosion lignin extracted from sarkanda grass, wheat straw, aspen wood and hardwood ammonium lignosulphonate are the most investigated [75]. Furthermore, those studies that concentrated on lignins emanating from the industry [96,107,109,112,113] focussed on the composition of the oil, but rarely considered the optimisation of phenols yield coming from pine, eucalyptus, and sugarcane. Hence, it is pertinent to research on the lignin pyrolytic chemical products of these biomasses.

2.4.2. Effect of heating rate on pyrolysis chemical products

Depending on the heating rate, pyrolysis operations can be called fast or slow [25,103]. The time and extent of heating affects the progression of the reactions and distribution of the generated products. Slow pyrolysis of biomass is carried out gradually (0.1-1^{o}C/s) and at proportionately mild temperatures between 300 ^{o}C to 400^{o}C, and the main product is char. However, increasing the temperature (> 400^{o}C), increased the yield of oil. On the contrary, at elevated heating rates, the yield of vapours is high, with a gas and liquids distribution that depends on the final temperature [97,114].

During lignin pyrolysis, slow heating rate enhances the cleavage the most of the functional groups that are not stable first with derived-monomers obtained having structures close to that of the monomer units [92]. Furthermore, the bio-oil resulting from slow heating of lignin could contain a high concentration of the desired chemical products (phenols) [115].

Fast pyrolysis is carried out at elevated heating rates and is aimed at maximising the yields of bio-oil, by inhibiting the secondary cracking of the primary products into incondensable gases [103,116]. Liu et al. [117] performed pyrolysis of fir and birch lignins at two different heating rates (10 and 40K/min) and found that more volatiles were produced with limited char formation as the heating rate increased. At a high heating rate, numerous ether and alkyl bonds connecting the phenol monomeric units cleaved at the same time, except the hydroxyl functional group attached to the aromatic ring that is greatly stable [118]. Whereas fast heating rates promote higher bio-oil yield compared to slow pyrolysis, a better selectivity of the chemical products

can be expected in the case of low heating rate. Therefore, both fast and slow pyrolysis of lignin were studied for phenols production.

2.4.3. Effect of temperature on lignin chemical products

Among the studies conducted to produce valuable chemical products from lignin pyrolysis, temperature is the major parameter investigated. The complex nature of lignin means the lignin pyrolysis mechanism and chemistry are different from the whole biomass [91] . Upon pyrolysis, lignin degrades into phenolic building blocks and smaller pyrolysis products, depending on the temperature applied. Therefore, it is pertinent to describe the thermal degradation mechanism of lignin.

2.4.3.1. Mechanism of Thermal Degradation of Lignin

Lignin consists of numerous types of interunit linkages, with the ether aryl linkage dominating the lignin structure [25,119]. During lignin pyrolysis, thermal energy is distributed among the internal degrees of freedom of the polymer network. This results in several competing thermal degradation reactions, during which different bonds dissociates at different temperatures, depending on the bond energies. A key step in the thermal degradation of lignin is the fission thermal bond rupture of the weaker (α- and β-alkyl-aryl ether) bonds [120]. Compare to cellulose and hemicellulose, lignin degrades span through a broad range of temperatures (200-500 ^{o}C), because the numerous chemical functions inherent in the structure of lignin differ in stabilities thermally and therefore, behave differently during heat treatment [35,110,118]. Consequently, it seems that a step by step pyrolytic means could be a measure to obtain high grade products, thus facilitating separations.

To understand the thermal decomposition mechanism that leads to the making of lignin chemical products, a number of studies used model compounds which showed

that lignin pyrolysis products are largely formed by a free radical mechanism [25,121]. Lignin analysis by thermogravimetric (TG) reveals that the decomposition (thermal) steps begins with dehydration at temperature < 200^{o}C [117] and water is the main product that is released from lignin. The primary stage of lignin pyrolysis is the conversion step and it covers a wide temperature range of 200-450 ^{o}C. The lignin weight loss is maximised within this range (specifically 370-400 ^{o}C), which exceeds those of cellulose and hemicellulose, reported in literature to be between 200-350 ^{o}C and 330-370 ^{o}C respectively [92]. In the main stage of lignin degradation, the release of most condensable vapours takes place within this range of temperatures, attributed to the nature of the alkyl substituents which are not stable, a few ether bonds connecting the monomeric units of lignin, and functional groups like the methoxyl groups (CH_3O-). Most alkyl side substituents are broken around the temperature stretch of 230-400 ^{o}C. Cleavage of the aliphatic chains or methoxyl groups from the lignin building unit can lead to the exchange of the methoxyl or alkyl substituent with methyl (CH_3-), hydroxyl (-OH) or hydrogen atom (H) groups [98,122,123]. C_1 chemical products such as methanol (CH_3OH) and methane (CH_4) are produced from the cracking of methoxy groups of the lignin phenyl propane aromatic units [99,124]. Formaldehyde (CH_3CHO) and formic acid (CH_3COOH), which are the C_2 chemical products, are obtained from the alkyl side chain fragmentation. Many phenols such as phenol and its derivatives, guaiacols, and syringols are produced in the primary pyrolysis stage [69,118,123,125].

In the pyrolysis of fir and birch lignins, Liu et al. [99] found that phenols where formed in the primary stage within the temperature ranges of 150-327^{o}C and 125-283^{o}C respectively. Murwanashyaka, et al. [126] reported that chemical products such as aromatic hydrocarbons, phenols and its derivatives are the major products

formed within the primary pyrolysis temperature ranges. Luo et al. [127] conducted an experiment on thermal decomposition of organosolv beech lignin and found that the primary stage which released phenols occurred in the range of 200-450^{o}C. It has been found that guaiacols formed at lower temperatures while products such as phenols, catechols and syringols were formed at higher temperatures. Jakab, et al., and Luo et al. [124,127] revealed that aldehydes such as vanillin and its derivatives are probably formed from the cleavage of beta-gamma carbon linkage (C_{β}-C_{y}) in the alkyl side chains with –CH_2OH or –COOH groups in gamma position.

The third lignin thermal degradation stage happens occurs at temperature lower than or equals to 450 ^{o}C which is associated with increase liberation of gases. At elevated temperature (approximately 600 ^{o}C), the cracking of the side chains connected to the benzene ring can generate carbon monoxide (CO), hydrogen (H_2), and methane (CH_4) [98]. With increase temperature > 600 ^{o}C, the polycyclic substances inherent in char rearranged and gases are released [99,128].

2.4.3.2. Studies on the effect of temperature on the pyrolysis yields

Several lignin types have been researched on to find out the influence of pyrolysis temperatures and the type of chemical products obtained. The influence of temperature on fast pyrolytic conversion of bamboo lignin extracted by the enzymatic mild acidolysis method (EMAL) was studied by Lou et al. [130]. They applied Py-GC-MS and found that lignin decomposition happened within a span of 250 ^{o}C to 600^{o}C. The resulting compounds were derivatives of p-hydroxyphenylpropanoid, guaiacylpropanoid, syringylpropanoid classified as 2,3-dihydrobenzofuran (DHBF) and phenols. At 600 ^{o}C, they obtained the largest amount of phenols, while the amounts of DHBF dropped with as temperature was raised. In a similar studies, Lou

& Wu [131] fast-pyrolysed enzymatic/mild acidolysis lignin (EMAL) from moso bamboo at different temperature regimes within a temperature stretch of 400 ^{o}C to 900 ^{o}C executed in a tubular reactor. They found that the highest phenols production was obtained at 600 ^{o}C. The same outcome was reported by Brodin et al. [107] after pyrolyzing Kraft *E-globulus* and birch trees lignins employing a step by step approach beginning at 200 ^{o}C until 900 ^{o}C. Between 200-300 ^{o}C small quantities of syringol, gauiacol were obtained. On increasing the temperature to 400 ^{o}C, they obtained a large amount of phenols. Beyond 700 ^{o}C, only char was dominant. Yang et al. [110] fast-pyrolysed wheat straw EMAL lignin in a Py-GC-MS at 500 ^{o}C, and generated guaiacyl, syringyl, and hydroxyphenyl monomeric phenols. The same outcome was reported by Trinh et al. [102] after pyrolysing wheat straw lignin residues recovered from a cellulosic ethanol process, performed in a gram scale pyrolysis centrifuge reactor (PCR) within a temperature range of 500-550^{o}C. Maximum yields of guaiacol, p-vinylguaiacol, and syringols were achieved at this temperature range. Jiang et al. [101] pyrolysed two Organoslv (Alcell and Asian) lignins using Py-GC-MS to research on the influence different temperatures between 400-800^{o}C on the yield distribution of phenols. They found that the highest yield of phenols was produced at 600^{o}C for the two lignin types, producing a maximum of 17.2 wt.% and 15.5 wt.% of total phenols for Alcell and Asian lignins respectively. The yields of lower molecular weight phenols continuously rose as the temperature was elevated due to the cracking of the lignin substituents through demethoxylation, demethylation, decarboxylation and dealkylation reactions. Overall, these studies have produced a majority of the phenolic chemical products within temperatures $\leq$ 600^{o}C mentioned in the lignin thermal degradation mechanism considered in section 2.4.3.1.

Considering the amounts of products produced according to the impact of temperature which were mostly less than 10%, attributed to partial transformation, pyrolysis involving the use of catalysts could improve depolymerisation to achieve high yield of chemical products of interest such as phenols considered in this study.

2.4.4. Effect of residence time on pyrolysis chemical products

This is the time volatiles remain in the hot part of the reactor and is a major factor in the extent to which vapour products are converted during thermal degradation of biomass. When volatiles are unstable at the reactor temperature, lengthy vapour residence time favours secondary reactions, with chars and low yield of liquid as the principal products [97]. The first is the cracking of the primary products, while the second is the recombination of the primary products. The properties of the chemical products are changed. Therefore, it is worthwhile to select a short residence time to limit secondary reactions of the vapours considering the products of interest from lignin pyrolysis which needs to be obtained in the primary pyrolysis stage. Alternatively, during pyrolysis of lignin at 400^{o}C and longer residence time, cracking of some substituents such as methoxy or methyl groups was found to occur [101].

2.4.5. Effect of reactor type, configuration and scale

Lignin has been studied in the last few decades using different pyrolysis reactor configurations to obtain chemical products. Generally, the most common reactor configurations employed for the pyrolysis of biomass materials include fluidised bed, rotary cone, auger/screw, and ablative reactors [103,114]. In most lignin pyrolysis studies, analytical pyrolysis techniques have been employed. For example, Pyroprobe-GC-MS, and thermogravimetric analyser linked to FTIR have been commonly used [96,108,110,129]. These analytical pyrolysis techniques enabled online analyses of

the produced volatile chemical products. Other reactor configurations reported in literature for lignin pyrolysis include fluidized bed reactor, tubular reactor furnace [107,131], microwave reactor [132–135]. A laboratory scale (200-400 g) pyrolysis centrifuge reactor was used by Trinh et al. [102]. Zhao et al. [136] used a tubular reactor made of quartz glass. A split-tube furnace (4g) was used by Ben & Ragauskas [109]. Choi & Meier [137] used a small fixed bed TI-mini fast pyrolyzer, Ma et al. [138] used a platinum coil pyrolyzer.

These pyrolysers were milligram, gram or kilogram-scales engaged to pyrolyse lignins of diverse origins under numerous circumstances which may have influenced lignin pyrolysis products. Therefore, it is hard to correlate the pyrolysis yields and discuss the influence of reactor configuration. None of the previous studies paid attention to the employment of the TGA-TD-GC-MS to research on the pyrolysis of lignins to produce phenols.

Choi & Meier [137] reported that milligram scale pyrolysis has limitations in providing detailed knowledge concerning the chemical product yields. Alternative pyrolysers could boost this shortcoming and therefore, the need to explore the pyrolytic transformation of lignin using larger scale reactors.

2.4.5. Effect of catalyst on lignin pyrolysis products

Pyrolysis of lignin just as in whole biomass pyrolysis generates a vast spread of multi-functional phenolics in insignificant amounts other than when catalysis is added [54]. The optimisation of all the parameters that influenced the pyrolysis chemical products yields explained above has been found to be insufficient [91]. Thus, increasing attention is being paid to pyrolysis of lignin over different catalysts to produce high yields of valuable chemicals. A catalyst is a substance which accelerates the pace of a

reaction to form the desired chemical products without it being affected [54]. The performance of the catalyst is affected by numerous conditions among which contact between the catalyst and the reacting substance is one [98]. Catalyst can be either be physically blended or impregnated with the reacting species and this has been demonstrated with many biomasses [98]. Reports of studies of reaction of biomass and catalyst revealed that both methods have a similar influence except that impregnation leads to greater synergy between the catalyst and the sample and hence, have more influence on the yield of chemicals product than the physical mix [98]. Therefore, impregnation was adopted in this study.

Catalyst has an impact on the amounts of end products which are char, gas, and oil, generated during lignin pyrolysis. For instance, pyrolysis of impregnated $ZnCl_2$ and NaCl as catalysts on biomass enhanced the formation of char [139]. Fierro, et al. [140] examined the impact of impregnated orthophosphoric acid on Kraft lignin in combination with other pyrolysis conditions. They observed that the acid catalyst produced more char yield than oil. Collard et al. [98] found the same outcome when they pyrolysed Nickel and Iron salts-impregnated lignin in a tubular pyrolyser.

Furthermore, most of the catalysis investigated on the pyrolysis of lignin have given more attention to the use of zeolites as catalysts with ZSM-5 as the main catalyst for deoxygenating lignin pyrolysis vapours into chemical products [89,96,109,127,136,137,141–143]. The monomers produced from zeolite catalysts are predominantly benzene, toluene, and xylene (BTX). Peng et al. [144] reported that a lower yield of phenols had been obtained with zeolite catalysts than the same pyrolysis of biomass without zeolite catalysts. Stefanidis et al. [145], also reported a drop in the yield of phenols using zeolite catalysts. Low yield and selectivity of phenols by zeolite catalysts has been reported by Lu et al. [147]. Zeolite catalysts are

known to be expensive and promote deoxygenation of organic compounds with more selectivity towards hydrocarbons such as BTX. Generally, these catalysts were examined to secure a bio-oil with properties close to conventional liquid fuels. BTX have a low value in contrast to other end products like phenols and its derivatives (phenol, vanillin, eugenol, catechol, guaiacols, syringols etc.) that can be obtained from lignin as shown previously in Figure 2-8. Therefore, zeolite catalysts do not appear as promising catalysts to produce marketable chemicals like phenols. Table 2-4 shows lignin pyrolysis products obtained with specific types of catalysis.

Table 2-1: Typical Chemical Products from Lignin Catalytic Pyrolysis

Chemical Products from Catalytic Pyrolysis of Lignin							
Lignin Name	**Catalyst**	**Pyrolysis Reactor**	**Temp. (ºC)**	**Yield range (wt. %)**	**Product**	**Char yield (%)**	**Reference**
Organosolv lignin	HZSM-5	Py-GC-MS	650	3.2-3.6	toluene, p-xylene	34	[148]
Alcell lignin	HZSM-5	Fixed bed micro-reactor	500-650	31-44	benzene, toluene, xylene (BTX)	Not specified	[141]
Aspen lignin	HZSM-5	Py-GC-MS	600	6.3-6.6	toluene, p-xylene	34	[148]
Kraft lignin	HZSM-5	Curie-Point Pyrolyzer	500-650	2.0-5.2	BTX	48-60	[108]
Alkaline lignin	MoO_3, NiO, Fe_2O_3, MnO_3, CuO	Pyroprobe pyrolyzer	650	<15 (peak area)[a]	Vanillin	50	[138]
Alkaline lignin	Ni-HZSM-5, Cu-HZSM-5, Fe-HZSM-5, Mo-HZSM-5, Co-HZSM-5	Pyroprobe pyrolyzer	500-650	<15 (peak area)[a]	BTX, phenols	50	[138]
Pyrolytic lignin	ZSM-5	Tubular reactor	600	9.20-31.57	BTX	Not specified	[136]
Kraft lignin	TiO_2	Pyroprobe pyrolyzer	550-600	>21	phenols	36-51	[88]
Alkaline lignin	NaOH, KOH, Na_2CO_3, K_2CO_3	Quartz fixed bed reactor	450	>30	Phenols	57	[144]
Wheat straw organosolv lignin	Nil	1kg/h bubbling fluidised bed reactor	500	7.0-11.0	Phenols	30-40	[100]
Alkaline lignin	Activated carbon	Microwave-assisted prolyzer	350-591	45 (peak area)[a]	phenols	29-56	[134]
Alkaline softwood lignin	TiO_2, CeO_2, ZrO_2	Py-GC-MS	500	26-37	Guaiacol derivatives	27-48	[149]

[a] in some studies, only peak area of the GC-MS analysis of the oil is reported. This result provides knowledge regarding product selectivity but cannot be treated as an actual mass yield.

Table 2-4 demonstrates that catalysts have precise targets for certain end products. The yield of the chemical products also differs according to the nature of the catalyst. Catalysts that influence the yield and selectivity for phenols and vanillin are relevant to this study.

Concerning pyrolysis, the manufacture of phenols studied in literature starts whole lignocellulose lignin and has been appraised by Amen-Chen, Pakdel, & Roy, 2001. Some studies devoted to pyrolysis of biomass have reported phenols production using alkaline or metal oxides as catalyst [146,147,150–154].

2.5. Alkaline Catalysts and Phenols Production

Alkaline catalysts are catalysts like the hydroxides and carbonates like NaOH, KOH, LiOH, $Ca(OH)_2$, K_2CO_3, $CsCO_3$, $RbCO_3$ etc. Alkaline catalysts can upgrade the amounts and selectivity of monomeric phenols, and they are common and inexpensive [60]. Many research studies have revealed that alkaline catalysts are effective for the transformation of lignocellulosic biomass materials to monomeric phenols in aqueous medium [5,151,155,156]. Water, methanol ethanol are the solvents, or combination of these solvents are used together with the alkali catalysts for the depolymerisation. Studies have shown that these catalysts selectively produce phenol, catechol and cresol vanillin etc. [157], but the yields (5-10%) were low [79]. Peng, et al. [144] studied the pyrolysis of alkali lignin mechanically blended with alkaline catalysts namely KOH, NaOH, Na_2CO_3, and K_2CO_3. The yields of phenols obtained exceeded 50% peak area based on the bio-oil content. This implies that the alkali catalysts could influence selectivity towards phenols production and can be further investigated to improve on the yields of phenols.

2.6. Metal Oxides Catalysts and Phenols Production

Metal oxides catalysts from group 2, 3 and the transition metal oxides have been reported to be promising catalysts in the production of phenols [158]. They include metal oxides such as Al_2O_3, CaO, Fe_2O_3, TiO_2, ZnO, MgO, CuO, MoO_3, NiO etc. Some of these catalysts have been investigated using pyrolysis and have been found to produce phenols. For example, Ma et al. [138] studied fast pyrolysis of alkaline lignin based on selective deoxygenation using oxides of transition metals and zeolites admixed with oxides of transition metals. They found that without a catalyst, a mixture of multi-chemical products was obtained which include phenol, vanillin, aromatic hydrocarbons and guaiacol with a low yield. The low yield could be improved by an optimisation approach. Therefore, it is important to explore these types of catalysts in lignin pyrolysis. Nair and Vinu [149] fast pyrolysed alkali softwood lignin directly mixed with synthesised TiO_2, CeO_2, and ZrO_2 catalysts. The mostly guaiacol derivatives were quantified by internal calibration. Their study resulted in total yield increases of 26-37%, with TiO_2 producing the highest yield increase.

Catalytic fast pyrolysis of poplar wood has been conducted with these types of catalysts (nano metal oxide catalysts-Fe_2O_3, CaO, ZnO, TiO_2, NiO and MgO) by Lu, et al. [146]. The pyrolysis of the poplar wood produced a 26.5% increase in phenols yield, while pyrolysis with the assorted catalysts yielded 13.0-32.6% amounts of phenols based on peak area, with the highest of 32.6% generated with NiO. The outcome of this study showed that metal oxide catalysts have selectivity towards phenols production.

Phenols production by lignin pyrolysis using titanium oxides as catalysts has been reported. Mante et al. [88] has researched on the pyrolysis of Kraft softwood lignin to compare the effects of two distinct types of titanium oxide (anatase and rutile) catalysts. They found that anatase catalyst influenced more phenolic production than the rutile catalyst. Pyrolysis of lignin from the various sources using titanium oxide catalyst through optimisation of the catalyst can further improve the selectivity for phenols. Therefore, titanium oxide is one of the catalysts that will be investigated in this study.

These studies reported the yields of phenols in terms of peak area. As mentioned in section 2.4, it is difficult to compare results because phenols yields based on peak areas are not actual yields but estimates. Rather, a quantification of the phenols yields using GC/MS and a calibration with standard compounds will be worthwhile. Based on the selectivity of the metal oxides towards phenols production, they can be investigated further to improve on their selectivity for phenol production, because their studies did not show any form of optimisation to maximise the yields and selectivity for phenol production.

2.7. Concluding Remarks

Phenols production appears as an interesting option to add value to lignin by-product obtained from different industries. Phenols can be obtained by depolymerisation using pyrolysis technologies, but a better understanding and an optimisation of this conversion are necessary. From the studies investigated on lignin conversion by pyrolysis, the following remarks can be assembled.

1. The operating conditions (temperatures, heating rate, reactor configuration) investigated could not produce a high yield (> 10 %) of chemical products of interest, which are phenols, requiring improvement.

2. Woody plant species such as aspen, oak, bamboo, birch, eucalyptus globulus, and non-woody plants such as wheat straw, and sarkanda grasses have been investigated. Because they differ in structural make up, diverse types of chemical products have been produced. Literature does not fully describe the pyrolysis chemical products of some woody and non-woody lignins such as pine, eucalyptus grandis, and sugarcane bagasse. Therefore, lignin chemical products from such plants will be investigated.

3. Among the valuable chemical products that can be produced from lignin through pyrolysis, the conversion to aromatic hydrocarbons mostly benzene, toluene, and xylene (BTX) has been extensively investigated compared to phenols. The BTX were obtained using zeolite catalysts as the primary catalysts. BTX have a relatively low market value while zeolites are relatively expensive. Phenols appear as more attractive options. However, in comparison with BTX production, very few papers have reported the use of catalyst to optimise phenols production by pyrolysis. Although the influence of the catalysts on pyrolysis mechanisms is poorly understood, alkaline catalysts and metal oxides appear as promising catalysts to increase phenols yield and selectivity.

   From the above general conclusions, it appears that many competitive and successive reactions are involved in lignin pyrolysis resulting in the formation of many assorted products with low yields. To increase the production of value-added compounds an improved knowledge of the pyrolysis mechanism is necessary. By promoting specific reactions, catalysts can significantly increase the yields and selectivity of product of

interest. However, for a better optimisation of the conversion, a better understanding of the influence of catalyst on pyrolysis pathways is also paramount.

2.8 References

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CHAPTER THREE

RESEARCH AIMS AND OBJECTIVES

3.1. Aims

The main aim of this study is to produce phenols from lignins using catalytic pyrolysis conversion technology. The complex structural and polymeric nature of lignin demands that the process follows the following steps.:

a. Detailed characterisation for identification of the physical and chemical properties of the selected and isolated lignins using both analytical and wet chemical techniques. This include quantification of the monomeric phenols by internal calibration with the new analytical method developed. The information from the lignin compositions is important for process optimisation.

b. Optimisation of phenols production through catalytic pyrolysis, with the approach consisting of three steps, which are:

   i. Comparison of phenols production from lignins extracted from three different biomasses to determine which feedstock has the highest potential for monomeric phenols production, influenced by the catalysts.

   ii. Screening of catalysts for selection towards further investigation into the production of phenols.

   iii. Optimisation of phenols production with the catalyst selected on the merit of performance to establish the optimal conditions (temperature/catalyst content couples) that maximised the yields of phenols.

3.2. Objectives

From the research aims, the influence of catalyst and the optimisation of process conditions were studied. This was achieved through the following specific objectives:

3.2.1. To investigate the physico-chemical characteristics of the lignins from various sources.

The lignins resulting from the pulp and paper and the emerging bioethanol industries are structurally modified, leading to physico-chemical complexities such as compositional variations, emergence of new functional groups and intermolecular bonds, impurity, odour etc. These physico-chemical complexities are challenging to researchers and has hindered the valorisation of lignin to value-added products. To overcome these challenges, researchers have devoted their efforts by exploring several wet chemical and analytical techniques, to reveal the true identities of the lignins. In this study, a novel analytical method known as the TGA-TD-GC-MS was used for the first time to quantify monomeric phenols by internal calibration from lignin pyrolysis. Aside the quantification of monomeric phenols, it has the advantage of mechanistic monitoring of the sample mass loss during pyrolysis. Furthermore, it can handle small sample size, with the generated condensable volatiles not requiring treatment before analysis by GC-MS. Hence, it is suitable for screening experiments, prior to optimisation of processes while reducing the number of experiments at larger scales. From the literature review, the use of TGA to study lignin the thermal behaviour has often been reported. Coupling TGA with volatile analyser such as MS or FTIR gives information about their composition but does not enable a quantification of individual compounds. Similarly, Py-GC/MS has recently been used as a technique to analyse the composition of lignin. In these studies, lignin is not characterised based on the yield of pyrolysis product but on the surface area (GC/MS) of these products. In this current study using TGA-TD-GC/MS, in addition to the

analysis of the thermal behaviour (TGA) of lignin, as well as GC/MS calibration with standard compounds, precise quantification of the products of interest was possible. From this objective, the physicochemical properties of the lignin samples of interest obtained through both analytical and wet chemical techniques provided possible ways to understand the mechanisms of conversion and the influence of catalysts on the reactivity of the various chemical functional groups. Some of the lignin samples obtained from the South African pulping industries have not been fully described and hence, this research provided an opportunity to characterise the lignin samples.

To accomplish this objective, nine lignin samples from various sources were characterised using a combination of several destructive and non-destructive techniques, each providing partial but complementary information. The presence of functional groups was determined to establish the purity and structure of the lignin samples. Proximate and ultimate analyses were conducted to elucidate the fundamental physical and chemical make ups of the various lignin. The analytical techniques (GPC, FTIR, and TGA-TD-GC-MS) were used to obtain information about the structure, functional groups, molecular weight and chemical composition (products) of the lignin samples. The research work undertaken to deliver this objective is elaborated in **chapter 4**.

3.2.2. To investigate catalytic pyrolysis of lignin obtained from different biomass sources to produce phenols.

Based on literature review, the chemical structures and the pyrolytic products distributions of lignins originating from different plant materials are substantially different and vary even within the same plant. The analytical pyrolysis method developed in this study was used to undertake the pyrolysis of three lignins types

originating from *E.grandis* (hardwood), pine (softwood) and sugarcane bagasse (herbaceous) plants. Pyrolysis of lignins obtained from these biomasses provided indication of the influence of biomass origin on the yields and selectivities of specific phenolic compound. This entails revealing the overall potential of these lignins in the production of monomeric phenols, and this has rarely been reported. Many researchers have shown that the pyrolysis of lignin without catalyst predominantly produced a complex mixture of phenolic compounds in low concentrations. However, when pyrolysed in the presence of a catalyst, the phenolic distribution changed dramatically. Several studies have reported catalytic pyrolysis of lignin to chemical products. However, the target has been to produce aromatic hydrocarbons, using expensive catalysts such as zeolites. While catalytic pyrolysis of lignin to produce phenols using available and relatively cheap catalysts such as metal oxides and salts of alkali and alkaline earth elements has been less commonly reported. The present studies contribute to existing knowledge by investigating into the phenolic production from lignins originating from the three types of biomass using the aforementioned catalysts.

To carry out this task, three lignin types originating from softwood, hardwood, and herbaceous plants was first impregnated with a defined amount of some selected metal oxides and salts, and then pyrolysed using TGA. To study the composition of the volatiles released during TGA, thermal desorption (TD) tubes were used for the volatile capturing at the primary devolatilization stages. It was followed by direct feeding of the volatiles to GC-MS for identification. The quantification of the chemical products was based on an internal standard calibration. The methodology followed to address this objective is detailed in **chapter 5**.

3.2.3. To undertake screening of catalysts and lignin from various sources for phenols production.

Based on literature review, there is a large variety of catalysts as there are lignin types. The aim of undertaking the screening study is to select the preferred lignin samples and catalyst combination to better understand the influence of the catalysts on the pyrolysis mechanism and yield in preparation for larger experiments. Priority was given to the lignin type (s) and catalyst (s) with the most effects on the yields and selectivity of phenol-derived compounds. As obtainable for **objective 2** based on literature review, majority of the screening studies have been concerned with the production of aromatic hydrocarbons instead of phenols. Based on the screening approach, the information about the range of catalyst concentration considered to maximise the yield of phenols was established.

To achieve this objective, three sugarcane bagasse lignins extracted using different isolation methods were impregnated with 12 different catalysts, including some metal oxides and alkali salts. The pyrolysis process followed to accomplish this objective is the same with the one that was used to accomplish **objective 2,** with the differences only in some of the lignin types. The study conducted to address this objective is detailed in **chapter 6**.

3.2.4. To investigate the effects of temperature and catalyst on the production of phenols from lignin.

With the preferred catalyst and lignin, maximisation of phenols production was ensued. From the literature, the yield and selectivity to phenolic compounds are influenced by numerous factors, key among which are temperature and catalyst-to-lignin ratio. However, the most frequently studied parameter in lignin pyrolytic

studies for optimisation of phenols production is temperature, known to always result in incomplete depolymerisation reactions. However, the application of catalyst would drive the reactions to competition, resulting in high yield and selectivity of the phenolic products.

In this approach, TGA-TD-GC-MS. was used to determine the catalyst concentration range at which the phenolic products were produced. These results obtained at milligram scale was used to define the limits of the range of the factors (temperature and catalyst content) that were optimised at gram scale using fast pyrolysis technology. The detail is addressed in **chapter 7**.

CHAPTER FOUR

Lignin Characterisation

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Titled: "Characterisation of Lignins from Different Sources by Appropriate Analytical Methods: Introducing Thermogravimetric Analysis–Thermal Desorption-Gas Chromatography-Mass Spectroscopy"

Authors: David Naron, Francöis-Xavier Collard, Luvuyo Tyhoda, and Johann Görgens.

Objective of the dissertation and summary of findings in the present chapter

This chapter addresses **objective 1**. Lignin samples obtained from black liquors resulting from the pulping of *Eucalyptus grandis* (*E.Grandis)*, pine (*Pinus Greggii*), and sugarcane bagasse by the Kraft, soda, soda-anthraquinone and sulphite processes were characterised for their physical and chemical properties using both wet chemical and analytical techniques. Lignin has different structure and composition depending on where it comes from. The isolation process impacts changes to the native lignins and therefore, information about the physico-chemical properties of the lignins provided direct evidence about its structure and degradation products. The understanding of the structural features of the lignins was key to the utilisation of the lignins in value-added application. Furthermore, this approach was a necessary step to achieve **objectives 2, 3, and 4**, which required the lignin samples to have acceptable properties prior to catalytic pyrolysis conversion to phenol-derived compounds. In this study, an analytical pyrolysis method referred to as thermogravimetric analysis-thermal desorption-gas chromatography-mass spectroscopy (TGA-TD-GC-MS) was applied to lignin pyrolysis for the first time to evaluate the chemical compositions

(syringyl, guaiacyl, and p-hydroxyphenyl- S, G, H) proportions of the different lignins and the results were compared with the one obtained by wet chemical method known as thioacidolysis. This was an important test to assess the reliability of the TGA-TD-GC-MS as an alternative quantitative analytical technique for the determination of the lignin monomeric proportions.

The results showed that depending on the plant species and isolation methods, 5.5-12.9 wt.% of the pyrolysis phenols monomeric products were quantified. Sugarcane bagasse lignins had more residual sugars than pine and *E.Grandis* lignins, and hence, significant amounts of furfural was produced. Softwood lignins had higher content of guaiacyl monomeric units compared to non-woody and hardwood lignins. With the TGA-TD-GC-MS method developed and used for lignin determination of monomeric (H, G, S) proportions, low S/G ratios with less variation (< 10%) for lignins from the same plant species were obtained when compared to thioacidolysis method. TGA-TD-GC-MS method enhanced depolymerisation by breaking different types of bonds in contrast to thioacidolysis, which selectively cleaved only labile aryl-ether bonds. With internal calibration of the GC-MS, the TGA-TD-GC-MS proved to be an effective alternative method for the determination of lignin monomeric compositions especially for lignin samples with less than 5% ash contents. Based on the reliable results obtained with the TGA-TD-GC-MS, it was utilised for comparison of phenols production from three different biomass origin (**objective 2**), screening of catalysts on three lignin types extracted from sugarcane bagasse (**objective 3**) and optimisation study, investigating the effects of two parameters (catalyst amount and temperature) on the production of phenols (**objectives 4**).

Declaration by the candidate

With regards to chapter 4-page numbers 87 to 135, the nature and scope of my contribution were as follows:

Nature of contribution	**Extent of contribution (%)**
Planning of the experiments	80
Execution of the experiments	100
Interpretation of the results	60
Writing the chapters	100

The following co-authors have contributed to Chapter 4 pages numbers 87 to 135 of this dissertation as follows:

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		Reviewing the chapter	40
		Interpretation of results to correlate with literature	20
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		Interpretation of results to correlate with literature	10
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		Interpretation of results to correlate with literature	10

Signature of candidate…….

Date……

Declaration by co-authors

The undersigned hereby confirm that the declaration above accurately reflects the nature and extent of contributions of the candidates and co-authors to chapter 4 pages number 87 to 135 in the dissertation

no other authors contributed to chapter 4 pages number 87 to 135 in the dissertation besides those specified above, and

potential conflicts of interest have been revealed to all interested parties and that are necessary arrangements have been made to use the material in to chapter 4, page numbers 87−135 of this dissertation.

Signature	Institutional affiliation	Date

ABSTRACT

Lignin is the most abundant natural source of renewable aromatic units and therefore, detail characterisation to unveil its chemical properties is a critical step for its utilisation. Nine black liquor samples from different plant origins namely sugarcane bagasse, *Eucalyptus grandis*, and *Pinus gregii* extracted from the Kraft, soda, soda-anthraquinone and sulphite pulping processes were considered. After lignin purification, when applicable, the samples were characterised by several common methods (wet chemical methods, Fourier Transformed Infra-Red spectroscopy, Gel Permeation Chromatography). Lignin monomer composition (H: G: S) was determined by thioacidolysis as well as a new pyrolysis method based on the use of an analytical set-up which couples Thermo Gravimetric Analysis (TGA) for lignin devolatilisation, the capture of released volatile compounds in thermal desorption (TD) tubes, and the quantification of the captured phenols by TD-GC-MS (gas chromatography-mass spectroscopy). The TGA-TD-GC-MS, with the use of internal calibration, allowed the quantification of 5.5-12.9 wt.% of monomeric products based on dry weight of purified lignin. Pyrolysis of sugarcane lignin resulted in significant yield of furfural, which was explained by the conversion of residual sugar. Pyrolysis of pine lignin gave the lowest yield of syringyl-type phenols, which was consistent with characterisation results (low methoxy content and absence of FT-IR band characteristic of syringyl unit). Pyrolysis method had the advantage to break different types of chemical bonds, which is likely to give a product distribution more representative of the lignin. With TGA-TD-GC-MS the monomer proportion for purified lignin from the same plant species were found to be very comparable (deviation lower than 10% for each unit). Compared to thioacidolysis (known to be selective towards bond cleavage and suspected to overestimate S content), TGA-TD-GC-MS gave lower S/G ratio for lignins with low ash content (< 5%). The TGA-TD-GC-MS method has demonstrated to be a good alternative technique to study the H: G: S proportions of lignins.

Key Words: Lignin, Thioacidolysis, TGA, TD-GC-MS, H/G/S Proportions

4.1. Introduction

Lignin is the second most abundant among the major constituents of lignocellulosic biomass materials, and is only surpassed by cellulose [1,2]. Lignin makes up 15-35% of lignocellulose on a dry basis [3]. It is a natural binding agent to fibrous lignocellulosic plant [3,4]. In addition, lignin protects the polysaccharides from destruction by fungi and bacteria [5]. Lignin has a complicated chemical structure [6], and is described as a multi-phenolic substance with an amorphous structure, produced by oxidative enzyme-initiated association of three different monomers namely p-coumaryl (H), guaiacyl (G), and sinapyl (S) units, which differ in the degree of methoxyation of the phenolic ring [7–9]. The guaiacyl lignin is dominant in softwoods biomass, while sinapyl and guaiacyl monomers are predominant in hardwoods [10]. Non-woody biomass contains significant amount of guaiacyl, syringyl and p-coumaryl structural units. The coupling of these different monomers by polymerization leads to the formation of a highly branched structure [11], with β-O-4-aryl ether bonds as the most common linkages [3,12]. There are also other linkages such as β-1, 4-O-5-diarylether, β–β-resinol, β-5-phenylcoumaran, α-O-4 and 5–5-biphenyl linkages (Supplementary Figure 1). These different linkages found in lignin make it a heterogeneous complex natural polymer. Under chemical or thermal treatment, these lignin linkages behave differently due to differences in bond energies.

The removal of lignin from biomass is of great interest in the pulp and paper industry and many emerging biorefinery concepts [13]. The objective is to selectively remove lignin by fragmentation and dissolution in order to recover cellulose, and to some extent hemicelluloses without severe modification to their structures[13]. Global

generation of lignin by the paper and pulp industry exceeds four hundred million tonnes per annum [14]. Additionally, the biochemical conversion of lignocellulosic plant materials into simple sugars, followed by fermentation to alcohols, which is one of the second generation biofuel technologies, is on the rise and is expected to result in the generation of large amounts of lignin [15]. Of this lignin, the majority is burned as a source of fuel with about 2% converted into chemical products and other commercial values [16]. However, these lignins can be used in value-added applications such as biomaterials and platform phenolic chemicals, as lignin is the only lignocellulosic component that is of aromatic phenolic structural nature, thus having the potential to replace current sources based on petro-chemistry.

Plants contain different quantities of lignin [17], and the physical and chemical properties of lignin vary depending upon the lignocellulose species [18], the age of the plants, the environment from which the plant is harvested, and the process by which the lignin is isolated [19,20]. The techniques available to isolate lignin from lignocelluloses typically result in structural modification of the native lignin, including its chemical composition and properties. Lignin isolation methods can be divided into the analytical types, e.g. Klason lignin, and the industrial types which include Kraft (sulphate) pulping, sulphite pulping, sulphur-free alkali (soda) pulping, organosolv pulping, steam explosion combined with enzymatic hydrolysis lignin, etc. [21,22]. These lignins differ in properties and reactivity with a multitude of variations in structural non-uniformity, functional groups, molecular weight distribution, odour, impurities, and chemical behaviour. These complexities and heterogeneity limit the interest in lignin exploitation, compared to the rapid advances in the exploitation of cellulose and hemicelluloses fractions to high value-added products [23–26]. Furthermore, uncertainty about the true structural and compositional makeups of

lignins, irrespective of significant progress in structural characterisation, has further limited the technological development of efficient conversion routes to high value chemical products [8]. Despite these challenges, there is increasing research interest to exploit lignin into various applications, through the development of cost effective biorefinery processes that maximise the economic benefits derived from lignocellulose [15,27,28]. Because of the structural and compositional differences inherent in lignins, linked to plant origins and isolation techniques, a better characterisation to optimise lignin conversion has become a critical step for development of competitive processes to exploit the properties of lignin for value added applications.

A number of approaches have been reported to study the characteristics of various lignins to identify their physico-chemical compositions [24,29–32]. Some wet chemical techniques have been developed to detail the lignin functionalities [23,33]. Besides the lignin functionalities, the lignin H: G: S proportions have been determined using the wet chemical methods such as nitrobenzene oxidation (NBO), acidolysis, thioacidolysis, derivatisation followed by reductive cleavage (DFRC) [34–38]. The lignin-derived fractions generated from these methods are analysed using the Gas Chromatography-Mass Spectroscopy (GC-MS). However, the wet chemical methods are considered time and labour intensive, and require large amounts of samples and a multitude of hazardous chemicals [37,39,40]. Concerning the H: G: S proportions, the wet chemical methods are selective towards bonds cleavage and generate relatively low amount of monomeric products due to incomplete degradation of the lignin inter-units [40,41]. Due to some of these limitations, some spectroscopic methods such as Nuclear Magnetic Resonance (NMR), Fourier Transformed Infra-Red (FTIR) and Ultra-Violet (UV) were used to detail the lignin functionalities

[23,24], as well as the H:G:S proportion [32,35,42,43]. However, some drawbacks of the spectroscopic methods include low sensitivity and weak spectra resolutions as a result of signal overlaps [40,44]. Despite the challenges associated with the application of these methods, their use has generated the information which forms the basis for our current understanding of the structure of lignin and its possible utilisation.

In recent past, pyrolysis based methods such as Pyrolysis-Gas Chromatography-Mass Spectroscopy (Py-GC-MS), and Pyrolysis-Gas Chromatography-Flame Ionisation Detection (Py-GC-FID) have been prevalent as a means to estimate H: G: S ratios of lignin samples [35,42,45–52]. The principle is to depolymerise lignin by thermal treatment at 500 ˚C or 600 ˚C under inert conditions, and to analyse the phenolic composition of the volatile products using the GC coupled to MS or FID detector used for (semi-) quantification [53–55]. Lignin pyrolysis usually results in char yield higher than 30%. Amongst the released volatiles, some products of incomplete depolymerisation (mostly dimers and trimers) are found in significant amounts [55]. Some of these products are not detectable with GC and only the monomer-derived compounds containing one single phenol ring are generally used for lignin characterisation. As a consequence, this method assumes that the monomer-derived fraction produced by pyrolysis is representative of the lignin structure. Another requirement of this method is to keep the methoxy substituents intact, in order to be able to identify the H, G or S origins of the produced phenol. As the methoxy substituents are known to be unstable at temperatures higher than 400 ˚C [56], the residence time of the volatiles in the hot part of the reactor needs to be as short as possible. Another option considered in this study could be to generate and remove the

volatile phenols from the reactor at lower temperature in order to limit secondary reactions.

With regards to the GC/MS analysis, most of the reported compositions have been based on relative surface area of the Total Ion Current (TIC) Chromatogram obtained by MS. However, due to differences in the response factors of the different types of phenol [47,57], it appears that a calibration of the GC/MS instrument for peak areas vs. mass amounts would be highly advantageous for a more accurate estimation of H: G: S ratio, and also to determine how much of the lignin is actually characterised.

In this study, the technical lignins from various pulping industries in South Africa were characterised using wet chemical and analytical methods namely gel permeation chromatography (GPC) and FTIR. The determination of the H: G: S composition of the lignins was performed using thioacidolysis and a new analytical technique described by Nsaful et al., 2015, involving thermo gravimetric analysis (TGA) coupled to a system to capture the phenol in thermal desorption (TD) tubes online and the TD off-line coupled to gas chromatography/mass spectroscopy, referred to as TGA-TD-GC-MS. Together with an estimation of H:G:S proportions thanks to internal calibration of the GC/MS, this technique allows the monitoring of the mechanistic pathways by TGA. Compared to Py-GC/MS, TGA-TD-GC-MS technique is performed with low heating rate and is likely to limit secondary reaction and produce phenols with structures close to the original monomer units. From the characterisation of the South African technical lignins isolated from pulping process, the impact of plant material, pulping and isolation methods on the lignin properties were elucidated.

4. 2 Materials and Methods

4.2.1. Materials

Nine black liquor samples were received from different South-African pulp mills as listed in Table 4-1. All abbreviations assigned to the lignin types have links to their plant origins and isolation methods. For samples from the same plant and isolation method, mill source was specified. Seven of the black liquor samples from the alkaline processes (Kraft/Soda) were separated by sulphuric acid precipitation, while two from sulphite process (not suitable for precipitation, see section 3.1) were dried as received. Precipitation was done according to methods adapted from Garcia et al. [60], using 98-99% sulphuric acid at a pH of 2. After 24 h, the lignins were recovered by centrifugation at 7000 revolution per minute for 10 min. The recovered lignins were washed with distilled water, centrifuged again and air dried until constant weight. The two samples from sulphite process will be called dried sulphite spent liquors, while the samples obtained from the alkaline processes (Kraft/soda processes) and precipitation (without further purification) will be referred to as dried acid precipitated spent liquors.

Table 4-1: Plant Origins, Isolation processes, Sources and Abbreviations of the samples

Biomass Origin	Isolation Process	Mill Source	Abbreviation
Sugarcane bagasse	Soda	MPact Felixton	S-S
Sugarcane bagasse	Soda-Anthraquinone	Sappi Stanger	S-SAQ
Eucalyptus grandis (E. grandis)	Kraft	Mondi Richardsbay	E-K-M
E. grandis	Kraft	Sappi Ngodwana	E-K-N
Mixed 50/50 *Pinus greggii* (*P.greggii*)/*E. grandis*	Kraft	Mondi Richardsbay	PE-K-M
P.greggii	Kraft	Mondi Richardsbay	P-K-M
P.greggii	Kraft	Sappi Ngodwana	P-K-N
E. grandis	High Yield Neutral Sulphite Semi-Chemical-Anthraquinone (NSSCAQ)	MPact Piet Retief	E-NSSCAQ
Mixed 45/55% *P. greggii/E. grandis*	Low Yield NSSCAQ	MPact Piet Retief	PE-NSSCAQ

4.3. Lignin Purification

The dried acid precipitated spent liquor samples from the alkaline processes (Kraft/soda) were re-suspended in distilled water containing 1 N sulphuric acid as a purification method based on a proportion of 1 g dried lignin to 200 ml of the acid solution. The lignin solutions were allowed to stand for 24 h, centrifuged, and washed several times with distilled water until ash contents < 5% were obtained. The purified lignins obtained were air dried, ground, sieved to particle size range of 106-425 µm, and stored in plastic bags prior to characterisation.

4.4. Analytical Methods for Lignin Characterisation

4.4.1. Proximate and Elemental Analyses.

Lignin samples were characterised by proximate analysis to determine the content of the moisture, volatile, fixed carbon and ash according to the ASTM-E-1131 method, using a Mettler Toledo TGA/DSC 1 thermogravimetric analyser. About 18±3 mg of each lignin sample was loaded onto a 600 µl alumina crucible and placed on the TGA

pan. The sequence of the heating was moisture removal at 110 ^{o}C, volatile removal at 900 ^{o}C under nitrogen, and fixed carbon combustion with oxygen at 900 ^{o}C. The organic elements of the lignin samples were determined by a combustion method using elemental analyser TruSpec Micro (LECO) after combustion of the lignin samples on a fused glass bead. The major inorganic elements in oxide forms (Na_2O, K_2O, SiO_2, MgO, CaO, Fe_2O_3, TiO_2, MnO, P_2O_5, Al_2O_3, and Cr_2O_3) of the lignin samples were analysed by X-Ray Fluorescence spectrometry (XRF Pan Analytical Axios PW44W/24) and the individual elements were expressed on weight percent basis.

4.4.2. Sugar Analysis

The sugar content in the lignin samples were determined according to NREL/TP-510-42618 method (Sluiter et al.2012) [62], by subjecting the lignin to acid hydrolysis in two steps: treatment of the lignin samples with 3 ml of 72% H_2SO_4 followed by dilution of the acid to 4% with 84 ml distilled water to solubilise the residual carbohydrates. After incubation at 30 ^{o}C for 1 h with 10 min interval of stirring and subsequent autoclaving at 121 ^{o}C, the acid hydrolysed solutions were filtered through sintered glass crucibles. The insoluble residues retained on the crucibles were washed with hot water, dried and weighed. The residual sugars namely xylose, glucose, arabinose and mannose were determined by high-performance liquid chromatography (HPLC) using Thermo Separations Product Spectra System equipped with UV2000, Shodex RI101 detector, and a Biorad Aminex HPX-51H column (300 x 7.8mm).

4.4.3. Molecular Weight Determination by Gel Permeation Chromatography (GPC)

The average molecular weight (M_w), number average (M_n) and polydispersity (M_w/M_n) of the lignin samples were determined by GPC. The acetylated lignin

samples obtained as described in section 2.3.4 were dissolved in HPLC grade tetrahydrofuran (THF) stabilised with 0.125% butylated hydroxytoluene (BHT), 2 mg/ml. Sample solutions were syringe filtered through 0.45 µm nylon filters prior to analysis. The GPC system consisted of a Waters instrument composed of a 1515 isocratic HPLC pump, a 717_{plus} auto-sampler, 600E system controller (run by Breeze Version 3.30 SPA), an in-line Degasser AF and a 2414 refractive index detector at 30°C. THF stabilised with 0.125% BHT was used as eluent at flow rates of 1 ml min^{-1}. The column oven was kept at 30 °C and the injection volume was 100 µL. Two PLgel (Polymer Laboratories) 5 µm Mixed-C (300 x 7.5 mm) columns and a pre-column (PLgel 5 µm Guard, 50 x 7.5 mm) were used. Calibration was done using narrow polystyrene standards ranging from 580 to $2x10^6$ $g.mol^{-1}$. All molecular weights were reported as polystyrene equivalents.

4.4.4. Functional Groups by Wet Chemical Methods

The functional groups present in the lignin samples was determined by wet chemical methods. The presence of methoxy groups were determined according to the modified Viebock-Schwappach procedure described by Chen (1992a) [63]. Lignin samples were reacted with 57 % HI at reflux temperature to form methyl iodide. The iodide was then treated with bromine, which liberated the iodine and converted it to iodic acid. The iodic acid was treated with potassium iodide, and the liberated iodine was titrated with standard sodium thiosulphate solution.

Hydroxyl groups as total, phenolic, and aliphatic hydroxyl groups were determined by the methods described by Chen (1992b) and Lai (1992) [64,65]. Prior to hydroxyl group determination, 0.5 g of each lignin sample was acetylated with 20 ml of pyridine and acetic anhydride in equal amount with constant stirring at room

temperature under nitrogen flow for 24 h. A volume of 100 ml of 0.1 M HCl solution was added to precipitate the lignin and to remove pyridine. The precipitate was centrifuged, washed twice with 100 ml of distilled water to remove HCl, vacuum filtered and freed from moisture by freeze-drying. The total hydroxyl group was determined by reacting 10 mg of the moisture-free acetylated lignin with 4 ml of 6.5 M H_2SO_4 by refluxing for 1 h. The acetic acid produced from the reaction was titrated with 0.05 N NaOH solution using phenolphthalein as indicator.

The phenolic hydroxyl group was determined by aminolysis of the acetylated lignin using a method adapted from Lai (1992) [65], by dissolving 10 mg of acetylated lignin in 1 ml of 1-methylacetonitrile-pyrrolidine (1:1, v/v) solution. The 1-acetylpyrrolidine produced was quantified by GC by taking samples of the reaction mixture at 30 min, and hourly until 7 h of total reaction time. The aliphatic hydroxyl group was determined as the difference between the content of the total hydroxyl and phenolic hydroxyl groups.

The carbonyl group was determined by the oximation method described by Zakis, (1994) [66]. In brief, 80 mg of each sample was dissolved in 2 mL of dimethylsulphoxide (DMSO) followed by a 5 mL addition of oximating solution and heated at 80 ^{o}C in a water bath for 2 hours. The solution was allowed to cool and the triethanolamine (TEA) excess was potentiometrically titrated with a 0.1 N HCl solution until the pH of 3.3 using Hanna Instruments HI902 potentiometric titrator. A control test was conducted at the same time without lignin samples.

The carboxyl groups were determined according to the aqueous titration technique described by Toledano et al. (2012). In brief, 0.25 g of lignin samples was reacted with 12.5 ml of 0.05 M NaOH solution. The homogeneous solutions achieved by

stirring for 3 h were titrated with 0.1 M HCl to a pH of 7 using a potentiometric titrator. The content of the carboxyl groups was calculated based on the difference between the amount of NaOH consumed and the initially added NaOH.

4.4.5. FTIR

The lignin samples were analysed using Fourier Transformed Infra-Red (FTIR) Spectroscopy. The lignin samples were pressed against the diamond crystal surface with a spring-loaded anvil of a Thermo Nicolet Nexus^{TM} model 470/670/870 FT-IR spectrometer equipped with ZnSe lenses. Spectra were obtained in Attenuated Total Reflectance (ATR) mode at a resolution of 4 cm^{-1} and a number of 32 scan per sample within the absorption bands in the 4000-600 cm^{-1} region. Assignment of the major absorption bands was based on literature [68–70]. The FTIR spectra were baseline corrected and their intensities were normalised based on the amount of phenolic hydroxyl group of the samples: Each signal was multiplied by a factor for the intensity of the phenolic hydroxyl band at 3390 cm^{-1} to be proportional to the phenolic hydroxyl group content of the corresponding sample as determined in section 2.3.4. To differentiate between the spectra pattern exhibited by the different lignin samples, Principal Component Analysis (PCA) was performed using Statistica software (Statsoft V12). The PCA was focused on the spectral regions ranging from 2000 to 800 cm^{-1}, where most of the significant information of the lignin samples gathered [68,71].

4.4.6. Lignin Monomer Composition by Thioacidolysis

Thioacidolysis was used to study the original monomeric composition of the lignin samples. Thioacidolysis was done following a protocol published by Foster et al. [72]. In brief, about 2 mg of purified lignin was placed in a screw cap test tube followed by

additions of 5 µL boron trifluoride (BF_3) diethyl etherate (2.5%), 20 µL (10%) ethanethiol (EtSH) and 175 µL dioxane. The mixtures were purged with nitrogen and heated at 100 ºC in a water bath for 4 h with gentle mix hourly. The reaction was terminated by cooling in ice for 5 minutes. A 150 µL of 0.4 M sodium bicarbonate was then added followed by additions of 1 ml of water and 0.5 ml of ethyl acetate. A phase separation between the acetylated lignin and water was obtained by centrifugation. The acetylated lignin samples were collected in 2 ml sampling tubes and the solvents were allowed to evaporate under a well-ventilated hood. 200 µL of acetone was added with two repetitions and further evaporated under the fume cardboard until completely dried. The dried organic extract were trimethylsylilated with N,O-bis(trimethylsilyl) acetamine (TMSA) by the addition of 500 µL of ethyl acetate, 20 µL of pyridine, and 100 µL of TMSA. The derivatised samples were incubated at 25 ºC for 2 h followed by the addition of 100 µL of acetone to each sample prior to injection into the GC-MS. Chromatographic separation of the derivatised samples was performed by injecting 1 µL of the TMS derivatives of the samples into the gas-chromatograph-mas-spectrometer (GC-MS) (Agilent 6890 N Agilent, Palo Alto, CA, coupled to an Agilent 5975 MS mass spectrometer detector) equipped with a Thermo Scientific TG-SQC non polar (95% dimethylpolysiloxane) capillary column (P/N 26060-1300) with the following dimensions: 15 m length, 0.25 mm ID, and 0.25 µm film thickness. The GC injector port temperature was set at 280 ºC operated in a split mode set at a ratio of 10:1. Helium at a flow rate of 1 $ml.min^{-1}$ was used as carrier gas. The oven was set to an initial temperature of 70 ºC, maintained for 2 min, and thereafter ramped at 1 °C/min to 76 °C, then at 8 °C/min to a final temperature of 300 °C, and then held for 5 min. The MSD was set to full scan mode (40 – 650 m/z) to record the mass spectral data. The ion source and the

quadrupole temperatures were maintained at 240 °C and 150 °C respectively. Peak identification was done by characteristic mass spectrum ions of 299 m/z, 269 m/z, and 239 m/z reflecting the S, G, and H monomers. The H/G/S ratios were determined by comparing the peak area of the characteristic peaks.

4.4.7. Analysis of Pyrolysis Volatiles by TGA-TD-GC-MS

The lignin samples were depolymerised based on a pyrolysis technique in order to study their composition through the analysis of the generated volatiles by adapting the method described by Nsaful et al. [58]. In this method, 10 mg of each lignin sample was pyrolysed from 30 ^{o}C to 600 ^{o}C at a heating rate of 10 ^{o}C/min in an argon (baseline 5.0, Afrox) atmosphere (70 mL/min), using a thermogravimetric analyser (TGA) Mettler Toledo TGA/DSC 1-LF1100 system. The lignin volatiles released from the TGA were captured with a stainless steel, conditioned thermo-desorption (TD) tubes, number C1-AAXX-5003 (MARKES International, UK supplied by Chemetrix (Pty) Ltd, South Africa). The TD tubes contained porous polymer sorbents called Tenax TA suitable for wide range of applications and in particular high-boiling phenolic compounds (n-$C_{6/7}$-n-C_{30}). After the capture of the volatiles, the trapped volatiles were released offline into the GC/MS with the aid of a thermal desorption system (UNITY 2). The volatile desorption was done in two stages involving tube and trap desorption. In the tube desorption stage, the tube was rapidly heated to a temperature of 300 ^{o}C within 10 min, with the removal of volatiles from the tubes facilitated by a flow of helium (baseline 5.0, Afrox) gas dispensed from a cylinder at the rate of 80 ml min^{-1} based on a split ratio of 4. The volatiles were then released to a cool trap environment conditioned at -10 ^{o}C. In the trap desorption stage, the trapped volatiles were desorbed by heating at 320 ^{o}C for 10 min under a helium gas flowing at the rate of 1.5 ml min^{-1} into the GC-MS through transfer lines. With the transfer lines

maintained at 200 ^{o}C to avoid condensation, the flow of the helium gas in the tube and trap desorption stages was guided in the opposite directions. To maintain oxygen- and a moisture-free environment within the system prior to analysis, a 3 min pre-purging was performed at room temperature with helium gas at a flow rate of 2 ml min^{-1}.

Chromatographic separation of the volatiles released was performed with an Agilent Technologies 7890A GC, coupled to an Agilent Technologies 5975C MS equipped with a ZB-1701 (Agilent Technology) capillary column (14% cyanopropylphenyl-methylpolysiloxane) with the following dimensions: 60 m length, 0.25 mm ID, and 0.25 µm film thickness. Helium grade 5.0 (Afrox SA) at a flow rate of 1.5 ml min^{-1} was used as the carrier gas under a steady pressure of 25 psi set in a split less mode. The GC oven was set to an initial temperature of 45 ^{o}C and was maintained for 10 min and thereafter ramped to 100 ^{o}C at a heating rate of 2 ^{o}C min^{-1} and then at a heating rate of 7 ^{o}C min^{-1} (14 min) to a final temperature of 260 ^{o}C. The MS was set to full scan mode within a mass range m/z of 20-500 to record the mass spectral data. MS ion source and the quadrupole temperatures were maintained at 230 ^{o}C and150 ^{o}C respectively. The MS transfer line temperature was kept at 280 ^{o}C. The volatile compounds obtained were identified using NIST 2011 library and by comparing the retention time with those of standard compounds. Quantification of the phenols produced in significant yield (>0.05 wt.%) was done by internal calibration. The internal standard used was 2-octanol and the calibration curve of the volatile compounds was made using standard compounds with purity ≥ 98% supplied by Sigma-Aldrich. 27 standard compounds were selected on the basis of their concentrations obtained in previous tests as well as published literature. The calibration of the GC-MS was done by preparing a stock solution of the standard compounds and diluted to 5 concentration points using GC-grade acetone supplied by

Sigma-Aldrich. 3 µL of the phenolic standard compounds solution and 3 µL of internal standard were injected into the TD tubes and desorbed into the GC-MS aided by helium gas at 80 ml min^{-1}. A total of 27 compounds identified as products of lignin pyrolysis were calibrated (average coefficient of determination of the calibration curves was $R^2 > 0.98$). For quantification of the volatiles captured on the TGA, the same procedure of injecting 3 µL of internal standard into the TD tubes was followed before the tubes were desorbed for GC-MS analysis.

4.5. Results and Discussion

In this study, the dried acid precipitated spent liquor samples from the alkaline processes were first purified to remove some of the inorganics and residual sugars. The impact of the sources and pulping/isolation techniques on the physico-chemical properties of the lignin types was subsequently determined. The proximate, elemental and sugar analyses revealed the organics, inorganics and sugar compositions of the different samples. With the modification of the lignin native structures during the pulping processes, the molecular weights and functional groups revealed the chemical structures and their changes, which can be used to assess the severity of the delignification. The two sulphite samples (E-NSSCAQ and PE-NSSCAQ) were not used in the functional groups, GPC and FT-IR analyses due to purity requirements (section 3.1). The phenolic chemical compositions of all the nine samples were studied by thioacidolysis and TGA-TD-GC-MS technique, and the estimation of the proportions of the monomeric units are discussed.

4.5.1. Proximate Analysis

The results of the proximate analysis of the dried acid precipitated spent liquors, dried sulphite spent liquors and purified lignins are detailed in Table 4-1. The ash contents

of the dried spent liquors were measured between 10.8 and 40.4 wt.% dry basis, except for the two sulphite samples (> 60 wt.% dry basis). For accurate characterisation of the organic content and further valorisation of these lignins, a purification step is highly recommended. Except for the two sulphite samples the purification step using 1 N sulphuric acid (section 2.2) allowed the removal of a significant fraction of the inorganic content of the samples, resulting in ash content between 0.9 and 4.5 wt.% dry basis and thus, a substantial concentration of the organic content.

For both dried acid precipitated and sulphite spent liquors, a careful analysis of the TGA curves revealed that the fixed carbon content could not be determined accurately, apparently because of the evolution of the inorganic elements of the samples during combustion. In the TGA proximate analysis method, fixed carbon was measured as the mass loss resulting from the combustion of the sample following the introduction of oxygen in the reactor. However, for some of the samples, the mass loss from combustion was followed by a mass increase (see Supplementary Figure 4-2), which revealed that another reaction was affecting the fixed carbon determination. The residual ash component in the crucible and the mass increase thereof during combustion, could only be explained by the oxidation of some of the inorganics present in the ash. In particular, Na which was used in salt form during the lignin isolation process was the main inorganic element of both dried acid precipitated and sulphite spent liquors (Figure 4-1). Its oxidation into Na_2O could have resulted in mass increase up to 8 wt.%. As a consequence of this phenomenon, the fixed carbon content was clearly underestimated and could not be reported. For the purified lignins, the same inorganic oxidation only slightly affected the fixed carbon determination because of the lower ash (< 5 wt.%) and Na content (section 3.3). The ratio (volatile

matter)/(fixed carbon) of the purified lignin was found to be between 1.7 and 2.2 which is small compared to biomass samples and therefore, a characteristic of lignin samples [73].

The two sulphite samples from Piet Retief had the highest ash content (60.3 and 69.6 wt.% dry basis) and were not subjected to further purification, as these sulphonated lignins do not undergo precipitation by mineral acid at any pH. The high solubility of sulphite lignins in water is due to the presence of sulphonic groups in their chemical structures [74]. Therefore, the two lignins were simply dried as received.

Table 4-2: Proximate Analysis, Elemental analysis, and Total sugars of Dried Acid Precipitated Spent Liquors, Dried Sulphite Spent Liquors, and Purified Lignins

Dried Acid Precipitated and Sulphite Spent Liquors (wt.% Dry basis)									
Sample Name	Volatile Matter	Fixed Carbon	Ash	C	H	N	S	Total Sugars	Purity
S-S	65.7	ND[b]	19.1	49.7	4.7	0.9	3.4	6.8	74.1
S-SAQ	56.4	ND[b]	14.4	46.7	4.7	0.4	2.9	11.1	74.5
E-K-M	66.1	ND[b]	10.8	54.1	4.8	0.0	4.4	2.8	86.4
E-K-N	59.2	ND[b]	19.4	50.5	4.2	0.2	4.0	3.3	77.3
E-NSSCAQ [a]	48.6	ND[b]	69.6	18.6	1.4	0.2	4.3	ND[c]	ND[b]
PE-K-M	64.5	ND[b]	31.4	41.1	3.8	0.1	6.9	3.2	65.4
PE-NSSCAQ [a]	58.3	ND[b]	60.3	20.9	1.9	0.4	7.3	ND[c]	ND[b]
P-K-M	64.8	ND[b]	40.4	35.5	3.4	0.2	6.6	3.1	56.5
P-K-N	47.4	ND[b]	30.3	34.9	3.2	0.1	3.3	3.7	66.0
Purified Lignin (wt.% Dry basis)									
Lignin Name	Volatile Matter	Fixed Carbon	Ash	C	H	N	S	Total Sugars	Purity
S-S	66.7	29.6	4.5	61.2	5.5	0.2	4.6	6.4	89.1
S-SAQ	66.7	30.7	2.0	61.2	5.5	0.3	3.0	10.1	87.9
E-K-M	65.9	34.8	0.9	62.9	5.6	0.2	4.6	0.4	98.7
E-K-N	63.4	36.8	0.9	63.9	5.6	0.2	5.6	0.0	99.1
PE-K-M	64.5	35.8	0.9	60.2	5.5	0.5	2.9	0.4	98.7
P-K-M	63.0	36.8	1.2	64.6	6.3	0.6	6.3	0.6	98.2
P-K-N	64.1	35.3	1.7	65.0	5.9	0.2	4.9	0.9	97.4

[a] : **The two sulphite samples were only air dried without acid precipitation.**

ND[b]: Not determined due to inorganic oxidation affecting the determination by TGA. ND[c]: Not determined due to non-suitability of the sulphite lignins using the NREL method. For calculation of purity, sugars and ash were assumed to be the only impurities present in lignin samples.

4.5.2. Sugar Analysis of Lignin Samples

It has been reported that the concentrations of residual sugars in lignin depend on the isolation and purification techniques applied, as well as the nature of the plant [75]. The sugars in the dried acid precipitated Kraft spent liquors of *E. grandis* and pine were in the range of 2.8-3.7 wt.% dry basis (Table 4-2). Purification reduced the sugar content of the wood samples to below 1 wt.% dry basis. The two un-purified samples

from sugarcane bagasse had the highest amount of total residual sugars when compared to the wood samples from the Kraft processes. Lignin in non-woody plants are linked to carbohydrates (cellulose and hemicelluloses) forming complexes, resulting in difficulties with complete separation of lignin from sugars during isolation process [76]. Considering the amount of residual sugars in the purified lignins, S-S and S-SAQ only slightly decreased (Table 4-2), apparently due to incomplete lignin carbohydrate complexes separation. The sugar contents of lignin samples obtained after acid hydrolysis and the ash contents determined by proximate analysis, as presented in Table 4-2 were assumed to be the two major impurities of the lignin samples. Therefore, the two parameters defined the purity of the lignin types investigated in this study. The purified lignins had purities ≥ 88 wt.% dry basis.

4.5.3. Elemental Composition

The inorganic elemental compositions of the samples are detailed in Figure 4-1. Some of the inorganic elements could originate from the plant species prior to isolation, while significant amounts of other inorganics can be introduced during the pulping process. It was observed that the acidic purification of the dried acid precipitated spent liquors decreased the inorganics contents. Sodium was the dominant inorganic element present in the dried spent liquors. It is known that most of the pulping processes involved the use of sodium salts such as NaOH, Na_2SO_4, Na_2S and Na_2CO_3, whose concentrations (>10%) vary according to the isolation techniques [30,74]. With the acidic purification method applied to the samples, the sodium content decreased from the ranges of 2.4-13.4 wt.% to 0.02-0.07 wt.%. Furthermore, the un-purified samples contained silicates within the range of 0.5-2.2 wt.%, which was more pronounced in S-S (2.2 wt.%) and S-SAQ (2.0 wt.%). Herbaceous plants and in particular sugarcane bagasse is known to contain more silicates than woods

[2,31]. After purification, the silicate content of S-S increased to 3.9 wt.%, signifying that the silicates concentrated during the purification process, while that of S-SAQ reduced slightly to 1.1 wt.%,. The amounts of sulphur (3-8 wt.%) in the dried acid precipitated spent liquors, dried sulphite spent liquors and purified lignins (Table 4-2) originated from the biomass, pulping chemicals and sulphuric acid that were used in the precipitation and purification stages. With the removal of most of the inorganics, the carbon and hydrogen contents of the purified lignins increased (Table 4-2). The values of the carbon and hydrogen contents obtained (59-64 wt. %, 5-6 wt. % respectively), for the purified lignin samples were within reported ranges [50,73,77]. With purification in place, and with the exception of the two sulphite samples, all other results in the subsequent sections were based on purified lignin samples.

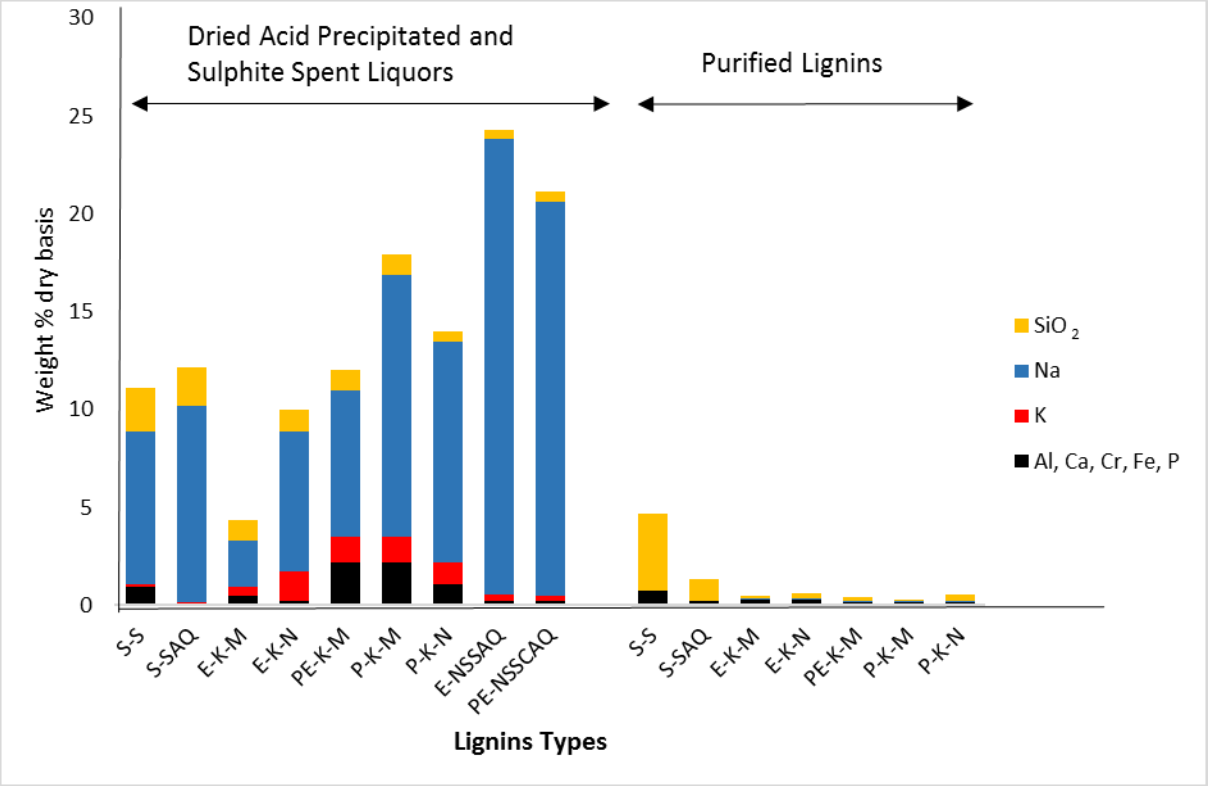

Figure 4-1: Inorganic Content of Dried Acid Precipitated Spent Liquors, Dried Sulphite Spent Liquors (E-NSSCAQ and PE-NSSCAQ), and Purified Lignins

4.5.4. Molecular Weight by GPC

The results of the number average (M_n), average molecular weight (M_w) and polydispersity (M_w/M_n) obtained for each lignin samples are shown in Table 4-3.

Table 4-3: Gel Permeation Chromatography (GPC) Results of the Molecular Weight of Lignin Samples

Sample Name	S-SAQ	S-S	E-K-M	E-K-N	PE-K-M	P-K-M	P-K-N
M_n g mol^{-1}	1721	2513	1398	1653	1573	2139	2244
M_w g mol^{-1}	3253	7779	2478	3178	3689	6957	8182
Polydispersity (M_w/M_n)	1.89	3.10	1.77	1.92	2.35	3.25	3.65

From Table 4-3, the molecular weights of the purified lignins ranged from 2478 to 8182 g.mol^{-1} and the number average molecular weights ranged from 1398 to 2513 g.mol$^{-1.}$ Although obtained from different pulping facilities, the Kraft lignins with common plant origins and isolation methods (E-K-M and E-K-N) and (P-K-M and P-K-N) had similar polydispersity (PD) values, signifying that the lignin depolymerised fractions had uniform chain lengths and therefore, similar molecular weight distributions [31]. This suggested that the severities of lignin fragmentations were similar during the Kraft process from the two different pulping mills. The average molecular weights and PD values for pine Kraft lignins were significantly higher than those of the *E.grandis* Kraft lignins, consistent with previous reports [75,78]. The chemical structure of lignins in softwood was predominantly made up of guaiacyl units (confirmed by high yields of guaiacol-related phenols obtained section 3.7.2), which are known to have more stable structure than lignins in hardwood [78]. In particular, the C5 position of the aromatic ring of the guaiacyl monomer is where some C-C linkages are formed between units, and these linkages are difficult to cleave

during isolations [34,39,78]. In addition, the β-aryl ether bonds in the synapyl units of hardwoods are easily broken during pulping processes, with less tendency to re-polymerise than the coniferyl units in softwood [29,39]. A significant difference in PD values was observed for the two sugarcane bagasse lignins (S-S and S-SAQ). The S-SAQ, which is a soda-anthraquinone lignin, had a PD value of 1.89, while S-S, which is a soda-only lignin, had a PD value of 3.10. The modification of the soda process by supplementing with anthraquinone that produced S-SAQ might have played a role in the molecular weight variations between S-SAQ and S-S. Indeed, it is known that through electron transfer mechanism, addition of anthraquinone catalyst promotes additional cleavage of β-O-4 linkages [74,79], explaining the lower molecular weight of S-SAQ.

4.5.5. Functional Groups

The lignin functional groups were analysed using methods described by Chen (1992a), Lai (1992) and Zakis (1994) [63,65,66]. Only carboxyl groups were determined using aqueous titration method described by Toledano, et al. [67]. The results of the content of the functional moieties obtained are shown in Table 4-4. The contents of carboxyl groups were between 4.6-7.2 wt.% and the carbonyl groups were relatively low (0.6-1.9 wt.%) for all the lignin samples (Table 4-4), consistent with reported values [23,43,67,81]. The contents of the methoxy and hydroxyl groups gave results which could be related to the H: G: S proportions among the lignin samples and the severity of the pulping process as described in the following sections (3.51 and 3.5.2).

Table 4-4: Results of Lignin Functional Groups (wt. % dry basis)

Lignin Name	OCH_3 (%)	COOH (%)	CO (%)	OH (%)		
				Total	Phenolic	Aliphatic[a]
S-S	22.0	5.3	0.5	14.3	5.4	8.9
S-SAQ	19.5	5.6	0.5	19.4	6.4	13.0
E-K-M	33.1	7.2	1.9	13.0	5.8	7.3
E-K-N	22.2	7.0	0.9	14.2	5.2	9.0
PE-K-M	28.6	6.5	1.4	13.1	5.8	7.3
P-K-M	13.0	6.0	1.3	14.5	5.9	8.6
P-K-N	15.0	4.6	0.6	11.7	5.7	6.0

[a] = Obtained by difference. The average standard deviation for methoxy, carboxyl, carbonyl, and hydroxyl groups were 1.0%, 0.1%, 0.1% and 0.5%, respectively.

4.5.5.1. Methoxy Groups

In Table 4-4, it can be observed that the methoxy groups of hardwood lignins were higher than those of pine and non-woody lignins which was attributed to their plant origins [46]. Lignins from hardwoods (mostly composed of G and S units), usually have higher methoxy group contents than in softwoods (mostly composed of G units), while non-woody lignin like sugarcane bagasse have values in-between those of hardwoods and softwoods [66,75]. The methoxy contents obtained for S-S, S-SAQ, E-K-N, P-K-M, and P-K-N were consistent with literature reports [66,75]. However, E-K-M hardwood lignin had a high methoxy content of 33.1%, while mixing this sample with the P-K-M resulted in a content of 28.6% for PE-K-M, which was higher than the typical reported range of < 25% [75]. A possible explanation for the overestimation of the methoxy groups could be related to the technique used during the pulping process, which might have caused the chemical group modification of the lignin native structure.

4.5.5.2. Total, Phenolic and Aliphatic Hydroxyl Groups

All the lignins had phenolic hydroxyl group contents within the range of 5.2-6.4 wt.%, consistent with previous reports [50,70]. S-SAQ had the highest amount (6.4 wt.%), which signifies intensive depolymerisation of the α- and β-O-aryl ether linkages during the isolation process, consistent with the GPC results for sugarcane bagasse lignin samples (Table 4-3). Indeed the degradation of α- and β-O-4 linkages increased the amount of phenolic hydroxyl groups due to the formation of free phenolic hydroxyl groups during the isolation process [46,82].

With regards to the aliphatic hydroxyl groups, S-SAQ had the highest amount (13.0 wt.%) due to the influence of carbohydrates as contaminants, consistent with the residual sugar results of S-SAQ (Table 4-2). This was also consistent with reports on the influence of residual sugars on the content of aliphatic hydroxyl groups [43,83]. In addition, S-SAQ had the highest amount of total hydroxyl group, mostly due to the high content of aliphatic hydroxyl groups.

4.5.6. FT-IR

With the FT-IR results, information on the chemical structure of the lignin samples could be obtained. The spectra overview regions (1800 – 800 cm^{-1}), where most of the relevant lignin spectra information resides from the FT-IR analysis of the lignins, are shown in Figure 4-2. The main observed bands were in accordance with what is usually reported in literature. The bands at 1712-1702 cm^{-1} showed the presence of unconjugated ketones and aldehyde groups [51,68]. Peaks at 1606-1510 cm^{-1} were ascribed to aromatic skeletal vibrations. Bands at 1461-1451 cm^{-1} are associated with methyl and methylene groups C-H bending. The presence of peaks within 1426-1424 cm^{-1} were related to ring-stretching modes strongly coupled with the C-H in-plane

deformation [68]. Peaks between 1367-1364 cm^{-1} were indicative of the C=O stretching of guaiacyl units. Similarly, peaks between 1327-1325 cm^{-1} were associated with the C=O stretching of guaiacyl/syringyl structures in lignin molecules [81,84]. The peaks at 1216-1211 cm^{-1} were associated with the guaiacyl structure in lignin molecules [51,68,81]. Peaks at 1044-1030 cm^{-1} were associated with C-O stretching of primary alcohols. Bands at 914-813 cm^{-1} were attributed to the C-H bending of guaiacyl and syringyl units, and specifically the band at 854 cm^{-1} was a C-H out-of-plane deformation band typical of the guaiacyl aromatic ring structure [70,78].

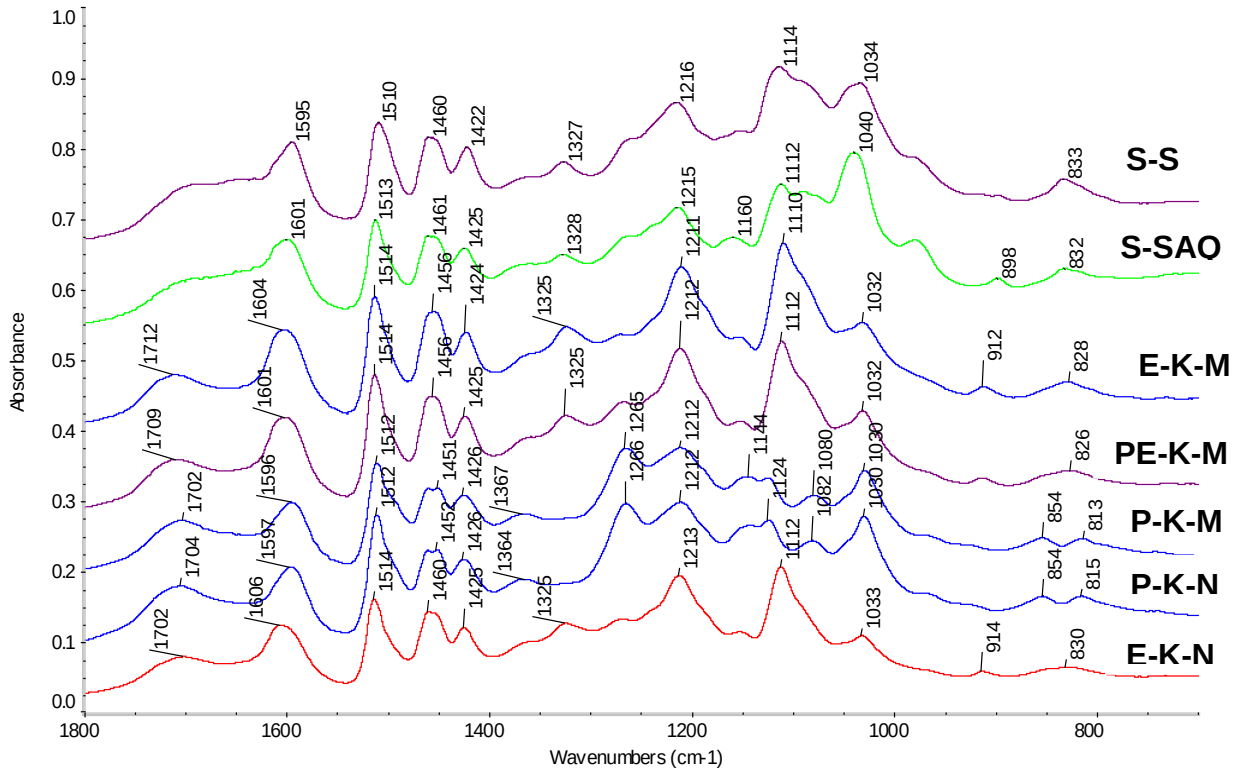

Figure 4-2: Fourier Transformed Infra-Red (FT-IR) spectra of the various lignins.

Principal component analysis (PCA) was used to correlate the chemical structures and compositions of the lignins. Principal components PC1, PC2 and PC3 explained 41.68%, 25.74% and 19.30% respectively, of the total variability in FT-IR spectral data among the lignins for the selected region. PC1 separates non-woody samples

(positive loadings) from woody samples. On PC2, no significant contribution to the grouping based on origin or isolation method was observed (see score plots for PC1 versus PC2 in Supplementary Figure 4-3). On PC3, samples containing only softwood lignin were separated with a marked negative loading. Therefore, the projection of the PCA results on PC1 and PC3 allowed identifying three different clusters based on sample origin, as illustrated in Figure 4-3.

Some specific bands were responsible for the separate groupings of woody lignins from the non-woody lignins on PC1. For example, the presence of peaks at 1044-1030 cm^{-1} corresponding to C-O stretching of primary alcohols were more intense for non-woody lignins than for woody lignins (Figure 4-2). The two non-woody soda lignins (S-S and S-SAQ), from sugarcane bagasse, had the highest amounts of residual sugars, and therefore, the two broad peaks at 1040 cm^{-1} and 1034 cm^{-1} contributed the most to their separations from the woody lignins, as well as their groupings together. Furthermore, S-S and S-SAQ had absence of peaks within 1712-1702 cm^{-1}, apparently due to severe modifications of their carbonyl functional groups. This was consistent with the contents of their carbonyl groups (Table 4-4), as the two soda lignins had the lowest contents.

On PC3, all samples containing hardwood or non-woody lignins had positive or close to zero loadings, while pine lignin (P-K-M and P-K-N) had negative loadings. The absence of bands within 1328-1325 cm^{-1} ascribed to C=O stretching of the syringyl units, together with more pronounced peaks within 1367-1364, 1266-1265 cm^{-1} and 854 cm^{-1} ascribed to C=O stretching, C-H in-plane deformations and C-H out-of-plane deformations of the guaiacyl units respectively, differentiated P-K-M and P-K-N from the other lignins.

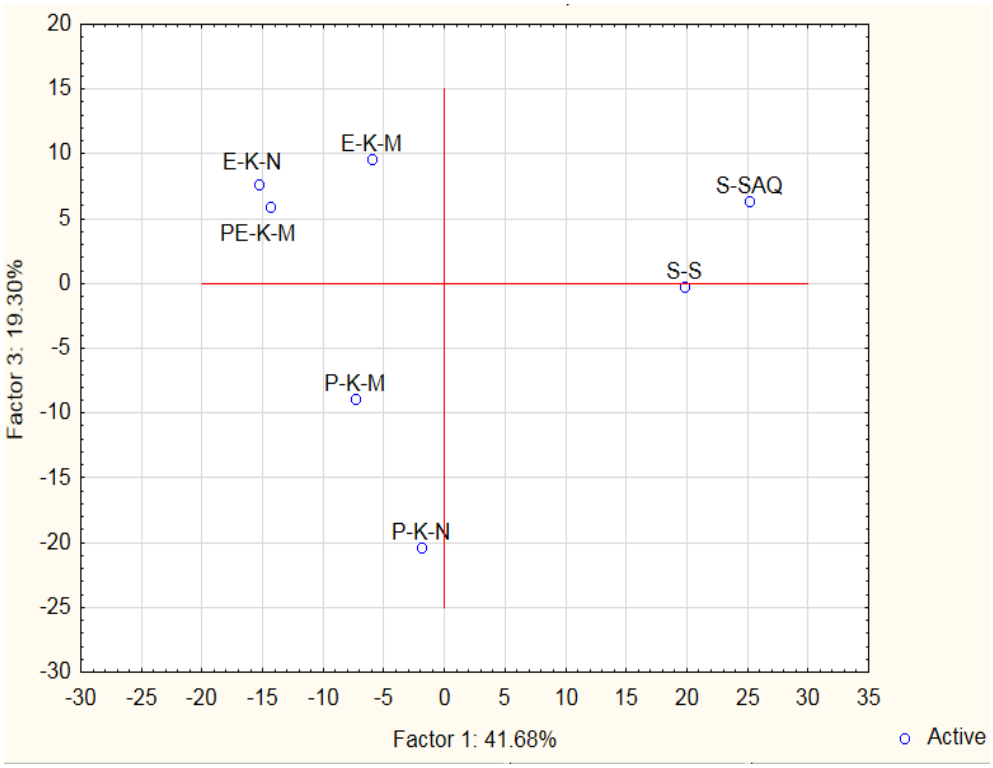

Figure 4-3: Principal Component Analysis (PCA) score plots of lignin types on Factors 1 and 3 (PC1 and PC3) based on Fourier Transform Infra-Red analysis of the lignins.

4.5.7. Lignin monomer composition

The lignin monomer composition was determined by both thioacidolysis and TGA-TD-GC-MS for the seven purified lignins (from Kraft and soda process) and the two sulphite samples. After an analysis of the monomer distribution obtained from each method, the differences between the two analytical methods were discussed.

4.5.8. Thioacidolysis

The syringyl (S), guaiacyl (G), and p-hydroxylphenyl (H) compositions were obtained after the cleavage of the aryl ether bonds (α-O-4 and β-O-4). The H, G and S fractions generated were subsequently analysed by GC-MS and the respective proportions are reported in Figure 4-4. From the results obtained, very low content of H unit (< 2%) were detected in eucalyptus and sugarcane samples. While this result was expected for eucalyptus [85], it is more challenging to interpret the sugarcane result as very

different Figures were reported from the thioacidolysis of non woody lignins. Thioacidolysis of non-woody lignins sometimes resulted in less than 5 %, and sometimes in greater than 10% of H units [86]. Pine samples had predominance of G units (88% and 81%), reflective of softwood lignins, with low S/G ratios (< 0.2). The S-S and S-SAQ lignins had more S units than G units with S/G ratios of 2.09 and 1.27 respectively. Similarly, the S/G ratio obtained from eucalyptus samples was close to 2, except for EKN. These relatively high S/G ratios were consistent with what is usually obtained for thioacidolysis of hardwood and non-woody lignins [35,87,88], but probably overestimated as reported in previous studies and discussed in section 3.7.3.

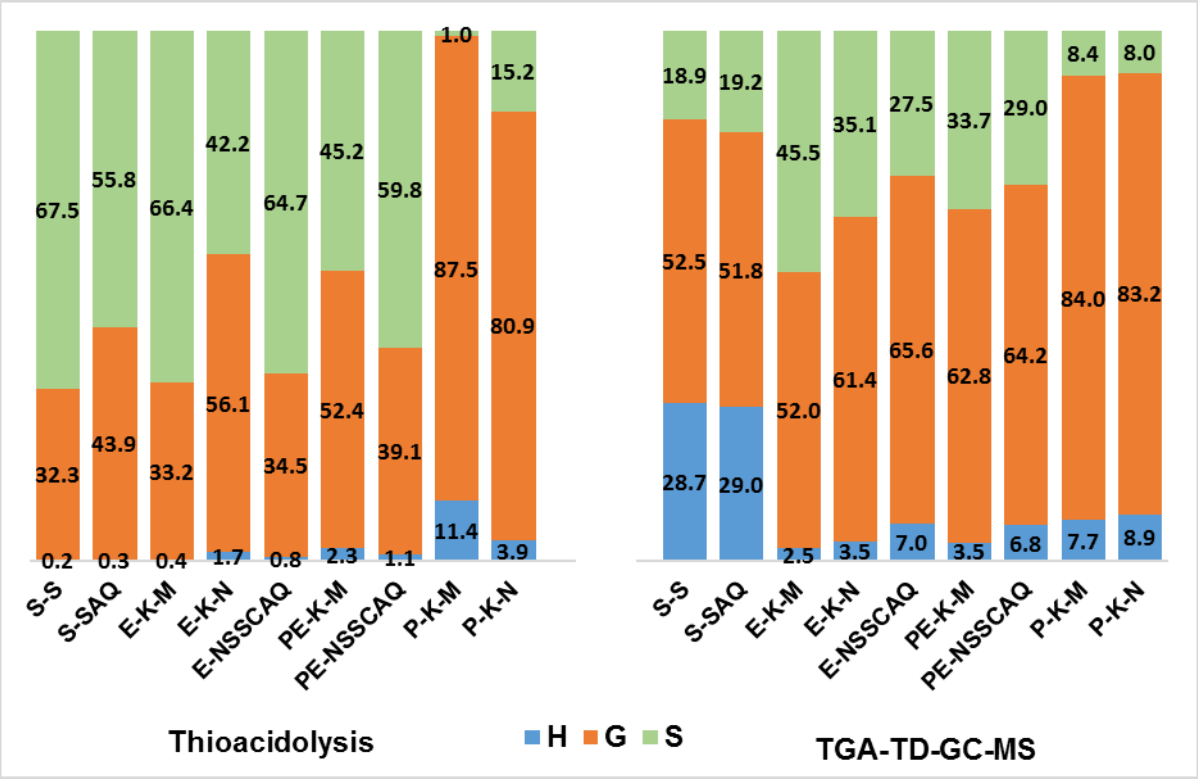

Figure 4-4: H: G: S Proportions of the Purified Lignins and Dried Sulphite Spent Liquors (E-NSSCAQ and PE-NSSCAQ) Obtained from Thioacidolysis and Thermogravimetric Analysis Thermal Desorption Gas Chromatography-Mass Spectroscopy (TGA-TD-GC-MS) Methods

4.5.9. TGA-TD-GC-MS

In the pyrolysis technique developed in this work, TGA was used for lignin depolymerisation. The thermal decomposition profiles, illustrated for the rate of weight loss (DTG), for the lignin samples are shown Figure 4-5. The thermogravimetric curves of the lignin samples are shown as Supplementary Figure 4-4. In Figure 4-5, all the lignins with the exception of the two sulphite samples (E-NSSCAQ and PE-NSSCAQ) had their maximum degradation rate within a range of 370-390 ^{o}C as usually reported in literature [56]. The two softwood lignins (P-K-M and P-K-N) had their maximum decomposition rate at 388 ^{o}C, while for the hardwood and non-woody lignins it was observed within the range of 370-380 ^{o}C. Indeed, softwood lignins are mostly composed of G units (as confirmed by FTIR curves section 2.3.5), linked by condensed C-C bonds, known to be more thermally stable than most of the bonds between monomer units in hardwoods and non-woody lignins [32,89]. The two sulphite samples showed very different degradation profiles with the lowest peak temperatures at 265 ^{o}C and 237 ^{o}C, probably due to the catalytic effect of the inorganic matter.

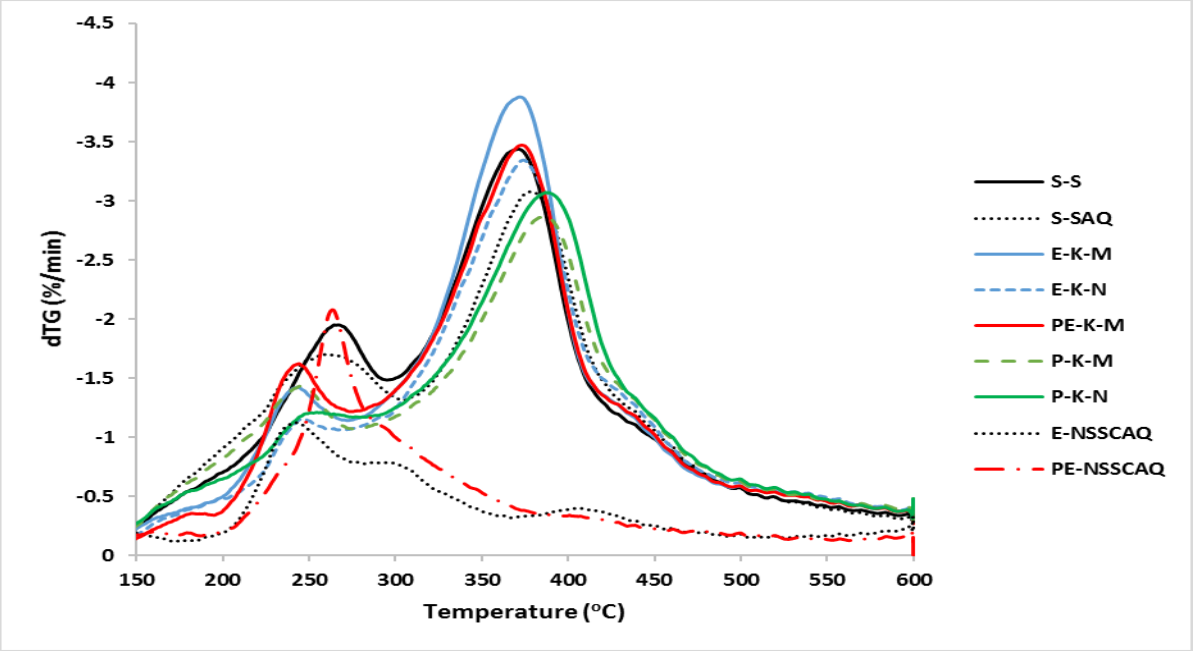

Figure 4-5: Differential Thermogravimetric (DTG) Curves of the Purified Lignins and Dried Spent Liquors (E-NSSCAQ and PE-NSSCAQ) during Pyrolysis Obtained under the Heating Rate of 1°C/min.

The phenolic volatiles generated by pyrolysis of the lignin samples using the TGA, were captured into the TD tubes, and quantified by GC/MS, as reported in Table 4-5. It is worth noting that S-S and S-SAQ produced the highest amount of furfural (1.66 wt.% and 3.06 wt.% respectively), which is consistent with their content in residual sugars (6.4 wt.% and 10.1 wt.% respectively). Indeed, sugars and in particular xylose are known to produce significant yields of furfural through pyrolysis [56]. While most of the lignin characterisation studies using pyrolysis are semi-quantitative analyses based on relative surface area of the Total Ion Current (TIC) chromatogram, this work was based on an internal calibration. With the use of quantitative method, the exact amount of lignin characterised could be established. From an extensive study of the fast pyrolysis products from 4 different lignins [55], oil yield between 39 and 55 wt.% was reported, with a water content of 36-44 wt.% and an oligomer content of 36-46 wt.%. Compared to dry lignin feedstock, the yield of monomer-derived compounds

identified as products from H, G, and S units (19 compounds) was in the range of 3.2-5.7 wt.%. This result highlights that in the studies using semi-quantitative methods, only based on monomer-derived compounds, the results could be based on less than 5% of the lignin sample. Another advantage of calibration is that it takes into account the different response factors of the various phenols, allowing an accurate quantification of pyrolysis products and thus, a better estimation of the H, G, and S lignin content (see section 3.7.3).

Compared to other pyrolysis techniques using a fluidised bed reactor or Py-GC/MS, the method developed in this study used relatively low heating rate (10˚C/min). The low heating rate was chosen in order to avoid a fast and almost simultaneous release of all the volatiles, likely to result in limited adsorption efficiency at the surface of the TD tubes. In the case of biomass, it is well accepted that higher heating rates promote the formation of volatile products and limit char yield [56], which is favourable to characterise as much as possible of the sample. However, with lignin samples, the influence of heating rate on char yield is less pronounced [90,91], and the use of very high heating rate does not appear to be critical. In this study for lignin samples with ash content lower than 5%, volatiles yield at 600 ˚C were in a range of 54-62 wt.%, slightly lower than what is usually observed for lignin fast pyrolysis at similar temperatures (52-70 wt.%) [2,55]. As the boiling points of the oligomers were expected to be higher than those of the monomeric phenols contained in them, low heating rate provided more time for further depolymerisation of some oligomers into monomer-derived compounds, which was likely to increase the proportion of monomer-derived compounds in the volatile fraction and thus compensate the lower devolatilisation of the lignin sample. In this study, the analysis of 26 aromatic compounds allowed the quantification of 5.5-12.9 wt.% of the dry lignin sample while

fast pyrolysis studies reported total yields of 3.6-6.8 wt.% (21 compounds) [55], and 5.6-18.4 wt.% (quantitative and semi-quantitative analysis of 75 compounds) [92].

Another advantage of low heating rates, together with TGA short residence time (<1 min), is that many phenols are released at relatively low temperatures (< 400 ˚C) before significant modification of the monomer structures, as illustrated by the relatively high yields of trans-isoeugenol (Table 4-5), especially from pine lignin (> 1wt.%). As a consequence, limited conversion of the methoxy groups was expected making the identification of their origin easier. For the example of G unit, a significant conversion of the methoxy group is known to happen by its substitution by methyl or hydroxyl group, which results in the formation of o-cresol or catechol moiety respectively [93]. Comparing the yields of the characteristic G compounds usually obtained in high yield (isoeugenols, 4-vinylguaiacol, ethylguaiacol, creosol, and guaiacol) from the various types of lignin, to those of o-cresol and catechol can give an indication of the extent of methoxy conversion. In this study the yield ratio (high yield G compounds)/(catechol + o-cresol) was in the range 5-10 showing a large fraction of the methoxy group remained intact, except for the lignin sample E-NSSCAQ. The lower ratio obtained for this sample (2.7) could be the consequence of extensive cracking of the methoxy groups due to catalytic effect of the inorganics present in particularly high content in this sample.

With regards to the product of typical phenol derived compounds identified by GC/MS listed in Table 4-5, the H: G: S proportions of the lignin samples were determined on the basis of the sum of the yields of the characteristic individual phenols and are detailed Figure 4-4. Significant content of guaiacyl units was observed with all the lignins comparable to other analytical pyrolysis reports with different types of lignin [32,35,51,52]. P-K-M and P-K-N from *P. greggii* had similar

H: G: S ratios that were characterised by a predominance of G units typical of what is reported in literature for softwood lignin [50,94]. The low content of the S unit in pine is consistent with the weak intensity of respective bands observed during FT-IR analysis. The hardwood lignins (E-K-M and E-K-N) had more G units (52% and 61%) respectively, than S units (46% and 35%) respectively, and lower amounts of H units (< 4%). The mixture of E-K-M and P-K-M lignin samples gave an intermediate monomer composition for PE-K-M as expected. The significant amount of the H units (29%) for sugarcane samples, were related to the H-G-S-type lignins from non-woody biomass [35,48]. The presence of p-coumaric acid and ferulic acid inherent in non woody lignin, converted through pyrolysis in H-type and G-type phenols respectively, could have resulted in a slight overestimation of H and G proportions [95,96]. Compared to eucalyptus samples, the higher and lower proportions of H and S units respectively were consistent with the lower content of methoxy groups in sugarcane lignin, as observed in section 2.3.4. Overall, the H: G: S ratios measured for the various lignin samples using TGA-TD-GC-MS agreed with reported compositions of lignins according to plant origins [32,50,54,97]. Compared to the other eucalyptus samples, the results obtained from the sulphite sample (E-NSSCAQ) were characterised by lower S amount compensated by higher G and H amount. The reason could be related to secondary reactions due to catalytic effect influenced by the high ash content, which might have converted some of the S-units to G-units, and G units to H units [89,98]. This signifies that the TGA-TD-GC-MS method would work better for lignins with lower concentrations of ash (<5%).

4.5.10. Comparison of Thioacidolysis, TGA-TD-GC-MS and other Pyrolysis Methods

A comparison between the methods used in this study for the estimation of the monomeric units (H, G, and S) was assessed. In the comparison, the amount of lignin

characterised (when applicable), consistency of results obtained with the same biomass, and the monomer proportions were considered. In terms of yields by TGA-TD-GC-MS method with GC/MS internal calibration, the product of typical phenol derived compounds represented 5.5-11.2 wt.% of dry lignin. On the other hand, such quantitative details can hardly be established using thioacidolysis. Thioacidolysis is a degradative method, which mostly resulted in low yield of monomeric products, as only monomers generated from the cleavage of aryl ether bonds are characterised [41,70]. In contrast, it is well known that pyrolysis at T>400 ˚C breaks not only aryl ether bonds, but also some C-C bonds [99] and thus, is likely to generate more monomer derived compounds.

The similarity between the proportions of the monomeric units (Figure 4-4) for the same biomass types was compared. Though it is well accepted that lignin composition depends on the age and the location of the plant, lignins obtained from the same species are expected to contain similar monomer proportions. For softwood lignins (P-K-M and P-K-N), the deviation in the thioacidolysis results for H, G, and S units were 7.5%, 6.6% and 14.2% respectively, in contrast to 1.2%, 1.0%, and 0.4% respectively, by TGA-TD-GC-MS. Considering the hardwood lignins, E-K-M had more S-units (66.4%), and E-K-N had more G units (56.1%) by thioacidolysis. The deviation in the results corresponded to 22.9% for G units and 24.2% for S units. With TGA-TD-GC-MS, the results for both G and S units deviated by less than 10%. For non-woody soda related lignins (S-S and S-SAQ), the deviation in the thioacidolysis results corresponded to 12% for both G and S units, while for TGA-TD-GC-MS, deviations of < 1% were observed. When the results obtained for lignin samples with low ash contents were compared, smaller deviations were observed with the TGA-TD-GC-MS method.

The monomer proportions (H, G and S) obtained with both methods were compared. In terms of H unit abundance, the main difference was observed for sugarcane bagasse lignins, with very low amount (< 0.4%) using thioacidolysis, while 29% were obtained by TGA-TD-GC-MS. Report has shown that 5% is the limit of H units produced from non-woody lignins by thioacidolysis [12]. However, other methods such as pyrolysis, FTIR, DFRC, and ^{31}PNMR have detected more than 5 wt.% [100], and even greater than 20% of H units from sugarcane bagasse lignin [36,100,101]. This signifies that the fraction of thioacidolysis products analysed by GC/MS is not representative of the lignin sample and that H units are probably underestimated with this method [102]. The relatively high value of H units (7.0%) obtained from E-NSSCAQ probably highlights a limitation of the TGA-TD-GC-MS method. Indeed, this result appeared as a result of secondary reaction, due to the catalytic effect of the inorganics, which had converted some of the G and S units to H units. As a consequence, lignin samples with relatively low ash content are required for this method.

With emphasis on the S/G ratios, the sugarcane and *Eucalyptus grandis* samples gave higher S/G ratios with thioacidolysis than those estimated from TGA-TD-GC-MS. Reports have shown that the thioacidolysis method is associated with incomplete degradation of the lignin inter-units, due to preferential depolymerisation of aryl-ether bonds associated with the syringyl (S) units [41,42]. This is likely to result in the overestimation of the S/G ratios [42]. On the other hand, pyrolysis methods extend the cleavage to include C-C bonds [99], resulting in the production of a group of monomeric units more representative of the lignin content [40,41], thus leading to lower S/G ratios than for thioacidolysis.

Finally, a substantial part of the result differences between methods using GC-MS can be due to the differences in response factors of the compounds used for the GC/MS characterisation. For example, from the TIC chromatogram of the GC/MS analysis of our calibration mixtures, compared to the internal standard, the response factors of phenol (from H unit), guaiacol (from G unit) and syringol (from S unit) were respectively 0.92, 1.34 and 2.49. This result means that when using semi-quantitative method, the S proportion is likely to be overestimated. Using these factors for the example of a bio-oil analysis containing 10% phenol, 45% guaiacol and 45% syringol, a semi-quantitative method would result in H: G: S ratio of 5:33:62. A similar trend was observed when comparing the response factors for the same compound with a methyl substitution in para-position of the hydroxyl group: 1.48 for p-cresol, 2.10 for creosol and 2.62 for 4-methylsyringol, thereby confirming the overestimation of S proportion by semi-quantitative method.

Table 4-5: Chemical Yields (wt. %, dry basis) obtained from Pyrolysis using Thermogravimetric Analysis Thermal Desorption Gas Chromatography-Mass Spectroscopy (TGA-TD-GC-MS)

Compound Name	S-S	S-SAQ	E-K-M	E-K-N	E-NSSCAQ[a]	PE-K-M	PE-NSSCAQ[a]	P-K-M	P-K-N
p-Hydroxyphenyl-type Phenols									
Phenol	1.48	0.78	0.04	0.07	0.03	0.08	0.03	0.22	0.32
p+m-Cresol	0.72	0.36	0.05	0.09	0.02	0.09	0.01	0.23	0.26
4-ethylphenol	0.49	0.24	0.00	0.00	0.01	0.00	0.01	0.00	0.04
Total	2.68	1.38	0.10	0.16	0.07	0.17	0.06	0.45	0.62
Guaiacyl-type Phenols									
Guaiacol	1.22	0.69	0.60	0.80	0.02	0.86	0.01	1.39	1.68
creosol	0.69	0.43	0.36	0.60	0.04	0.60	0.01	1.15	1.39
4-ethylguaiacol	0.34	0.29	0.26	0.28	0.13	0.28	0.12	0.33	0.34
4-vinylguaiacol	1.92	0.72	0.29	0.33	0.20	0.42	0.15	0.77	0.91
Eugenol	0.02	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.04
4-propylguaiacol	0.02	0.01	0.01	0.02	0.01	0.02	0.00	0.03	0.04
trans-isoeugenol	0.57	0.26	0.41	0.56	0.21	0.63	0.17	1.07	1.18
Isoeugenol	0.08	0.03	0.05	0.07	0.02	0.07	0.02	0.12	0.13
Acetoguaiacone	0.06	0.03	0.04	0.05	0.02	0.04	0.02	0.08	0.08
3-hydroxy-4-methoxyacetophenone	0.02	0.01	0.02	0.02	0.01	0.02	0.01	0.03	0.03
Total	4.92	2.48	2.05	2.74	0.65	2.95	0.51	4.99	5.82
Syringyl-type Phenols									
Syringol	0.98	0.39	1.01	0.82	0.04	0.91	0.04	0.18	0.19
4-methylsyringol	0.46	0.23	0.48	0.47	0.05	0.41	0.04	0.08	0.11
4-allylsyringol	0.03	0.01	0.02	0.01	0.01	0.02	0.01	0.00	0.00
Acetosyringone	0.30	0.28	0.27	0.27	0.18	0.26	0.13	0.23	0.23
Total	1.77	0.92	1.79	1.57	0.27	1.59	0.22	0.50	0.54
Sugar Derived Compound									
Furfural	1.66	3.06	0.53	0.45	0.00	0.45	0.00	0.40	0.52
Other Aromatic Compounds									
Toluene	0.33	0.14	0.03	0.05	0.02	0.04	0.02	0.09	0.12
Anisole	0.05	0.03	0.00	0.00	0.01	0.00	0.01	0.00	0.01
4-methylanisole	0.13	0.06	0.00	0.01	0.00	0.01	0.00	0.02	0.02
o-cresol	0.24	0.13	0.02	0.04	0.01	0.04	0.00	0.09	0.11
2,4-xylenol	0.09	0.04	0.01	0.02	0.00	0.02	0.00	0.05	0.06
3-methoxycatechol	0.57	0.36	0.69	0.59	0.00	0.82	0.00	0.17	0.11
Catechol	0.42	0.28	0.24	0.35	0.00	0.31	0.00	0.78	0.57
Total	1.82	1.03	1.00	1.05	0.04	1.24	0.03	1.21	1.00

[a] E-NSSCAQ and PE-NSSCAQ are dried sulphite spent liquors while the other samples are purified

4.6. Conclusion

Nine lignin samples from different sources were subjected to various common characterisation methods to investigate their chemical compositions. A new pyrolysis technique involving TGA, and TD-GC-MS was used in the estimation of the H, G, and S proportions of the lignin samples and compared with thioacidolysis method. Depending on the plant nature and for lignin with low ash content, 5.5-12.9 wt.% of the pyrolysis products were quantified. The residual sugars present in sugarcane lignin resulted in the detection of significant amount of furfural. Compared to non-woody and hardwood lignins, the higher content of G unit in softwood lignin, evidenced by FTIR analysis, was confirmed by the highest proportion of G-type phenols obtained by TGA-TD-GC-MS. The new pyrolysis method gave lower S/G ratios and led to results with smaller deviations for lignins from same biomass than thioacidolysis. Contrary to thioacidolysis which only cleaves aryl ether bonds, pyrolysis method breaks different types of bonds. Through improved depolymerisation and with the help of GC/MS internal calibration, the results of this study have demonstrated the effectiveness of TGA-TD-GC-MS as an alternative to study the H: G: S proportions of lignins with low ash content.

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CHAPTER FIVE

COMPARISON OF PHENOLS PRODUCTION FROM CATALYTIC PYROLYSIS OF HARDWOOD, SOFTWOOD, AND HERBACEOUS LIGNINS

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Titled "Influence of impregnated catalyst on the phenols production from pyrolysis of hardwood, softwood, and herbaceous lignins"

Authors: David Naron, François-Xavier Collard, Luvuyo Tyhoda, and Johann. F. Görgens.

Objective of dissertation in this chapter

This chapter specifically addressed **objective 2**: The yields of phenols and selectivity to specific phenolic compounds from the catalytic pyrolysis of three type of lignin isolated from eucalyptus, pine, and sugarcane bagasse were compared. The three types of lignins were selected following the significant amounts of monomeric phenols obtained with the analytical method, named as TGA-TD-GC/MS, as described for determination of monomeric phenols yields in Chapter 4. The lignins were impregnated with two metal oxide catalysts (Al_2O_3 and ZnO) and two hydroxide catalysts (NaOH and KOH) catalysts, with amount equivalent to 1 wt.% of the lignin mass. The TGA-TD-GC/MS was applied here to catalytic pyrolysis experiments, conducted at 600 ^{o}C, at a heating rate of 10 ^{o}C/min. The results of the monomeric phenolic yields obtained from the three lignin types revealed that the catalytic effects were more pronounced for sugarcane bagasse and hardwood lignins than pine lignin due to structural differences. That is the structure of pine is connected by condensed carbon-carbon bonds, which are more difficult to break than the mostly ether bonds inherent in the structures of both *E. grandis* and sugarcane bagasse lignins. In addition, following the release

of more phenols from sugarcane bagasse lignin than from both *E-grandis* and pine, it was selected for subsequent investigations to achieve **objectives 3 and 4** in Chapters 6 and 7.

Candidates Declaration

With regards to chapter 5, page numbers 139 to 168 of this dissertation, the nature and scope my contribution were as follows.

Nature of contribution	**Extent of contribution (%)**
Planning of the experiments	60
Execution of the experiments	100
Interpretation of the results	70
Writing the chapter	100

The following co-authors have contributed to Chapter 4 pages numbers 139 to 168 of this dissertation as follows:

Name	e-mail address	Nature of contribution	Extent of contribution (%)
François-Xavier Collard	fcollard@sun.ac.za	Planning of the experiments	30
		Reviewing the chapter	30
		Interpretation of results to correlate with literature	10
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		Interpretation of results to correlate with literature	10
Johann F. Görgens	fgorgen@sun.ac.za	Planning of the experiments	10
		Reviewing the chapter	10
		Interpretation of results to correlate with literature	10

Signature of candidate…….

Date…….

Declaration by co-authors

The undersigned hereby confirm that the declaration above accurately reflects the nature and extent of contributions of the candidates and co-authors to chapter 4 pages number 139 to 168 in the dissertation

no other authors contributed to chapter 4 pages number 139 to 168 in the dissertation besides those specified above, and potential conflicts of interest have been revealed to all interested parties and that are necessary arrangements have been made to use the material in to chapter 4, page numbers 139 to 168 of this dissertation.

Signature	Institutional affiliation	Date

Abstract

The production of phenols through catalytic pyrolysis of different types of lignin was investigated. Samples from Eucalyptus (hardwood), pine (softwood), and sugarcane bagasse (herbaceous) were impregnated with the catalysts, Al_2O_3, ZnO, NaOH and KOH, in quantities equivalent to 1% of the lignin mass. Pyrolysis was conducted using thermogravimetric analyser (TGA), and the released phenols were captured in thermal desorption (TD) tubes for quantification by gas chromatography/mass spectrometry (GC/MS). From the TGA profiles, some modifications in the primary mechanisms were observed, especially with the hydroxide catalysts. In comparison to non-catalysed lignin pyrolysis, KOH produced the most statistically significant effect on the total phenols yields from sugarcane bagasse (S-S) lignin, with increases up to +26%, while NaOH increased the yield from Eucalyptus (E-K) lignin by +40%. Syringol was the main S-type phenol product, with the highest yield increase by NaOH from E-K lignin (+90%) and a final yield of 1.86 wt.%. NaOH also produced the highest yield increases of G-type phenols from E-K lignin, especially 4-vinylguaiacol (+39% and yield of 2.8 wt.%). The increased production of primary compounds (S-type and G-type) by these hydroxides was probably correlated with the enhanced depolymerisation in the first decomposition stages, as observed by TGA. Oxide catalysts had limited effects on the production of S-type and G-type compounds but were more selective towards the production of P-type phenols, especially ZnO with S-S lignin (+36%) due to the enhancement of demethoxylation reaction.

Key words: pyrolysis, lignin, catalysis, impregnation, phenols

5.1. Introduction

Lignin is the second most abundant component of lignocellulosic biomass and is widely available as by-products from the pulping industry and emerging bioethanol productions. It is generally burnt to produce process steam and energy within the processes that generate it [1]. In the context of biorefinery development, a more sustainable and economical use such as conversion to value-added chemical products would be needed [2]. Lignin is a complex three-dimensional amorphous aromatic biopolymer composed of p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units [3]. The main difference in the three lignin monomers is the number of methoxy groups attached to the benzene ring. The proportion of the H/G/S monomers in lignin depends on the type of biomass. Hardwood lignin is composed of mostly the syringyl and guaiacyl monomers, softwood lignin is predominantly made up of guaiacyl monomers, and herbaceous lignin consists of syringyl, guaiacyl, and p-hydroxyphenyl monomers. The monomeric units of lignin are connected by C–O-C aryl ether bonds (β-O-4, α-O-4, 4-O-5) and C-C bonds (5-5, β-1, β-β), of which β-O-4 is the most common linkage [4], resulting in the formation of a very complicated lignin structure. In addition, the structure of industrial lignin depends on the method used to isolate it (Kraft, soda, sulphite, organosolv, steam explosion, etc.) from the lignocellulosic biomass.

Lignin phenolic nature and its availability makes it a potential resource to produce wide variety of phenolic and aromatic chemicals [5]. Several conversion technologies namely, chemical (base catalysed, acid catalysed, metallic catalysed, ionic liquids-assisted, supercritical fluids-assisted etc.) and thermochemical (pyrolysis, gasification, combustion, hydrogenolysis, etc.) have been developed to convert lignin to value-added chemical products [5,6]. Among them, pyrolysis is one of the most cost

effective methods for transformation of lignin to phenols [1,5]. Phenolic compounds like syringol, guaiacol, phenol, alkylphenols, isoeugenol, vanillin, cresols, etc. are chemicals used in the production of fuels, phenols resins, pharmaceutical products, cosmetics, perfumes etc. [7,8]. Phenol and vanillin have market

values around 1 500 US$/ton, and > 10 000 US$/ton respectively, while some other phenolic compounds have market values around 5 000 US$/ton [2]. During pyrolysis, the yields and selectivity of the phenolic compounds depend on several factors namely lignin type, reaction temperature, heating rate, volatiles residence time, and reactor configuration.

Generally, pyrolysis of lignin results in the production of a complex mixture of phenolic compounds whose yields are very low [9]. Therefore, catalytic pyrolysis has been considered to improve the yields and selectivity to specific phenolic compounds. Most of the catalytic pyrolysis studies for the production of phenols have concentrated on one or at most two particular types of lignin. Ma et al. [10] investigated the pyrolysis of alkali softwood lignin, in a micro-scale fast pyrolyser at 650 ^{o}C using metal oxides together with several zeolite-related catalysts with lignin-to-catalyst ratio of 1:4. Their main interest was selective deoxygenation of the phenols derivatives to aromatic hydrocarbons. Some of the catalysts like NiO and CuO increased the selectivity of guaiacol and vanillin by 25% and 35% respectively, (based on GC/MS surface peak area), as compared to the non-catalytic conversion. Nair and Vinu [11] studied the catalytic fast pyrolysis of alkali softwood lignin using CeO_2, ZrO_2, and TiO_2 (sol-gel and Aeroxide). The yields of guaiacol-related phenolic compounds were increased from 18 wt.% to 26-37 wt.%, with the sol-gel TiO_2 catalyst (lignin-to-catalyst ratio of 1:10) proving to be the best catalyst. Peng et al. [12] studied the effects of Na_2CO_3, K_2CO_3, NaOH and KOH on the pyrolysis of purified alkali wheat

straw lignin extracted from black liquor and a commercial alkali (unknown type) lignin in a fixed bed pyrolysis reactor at 450 ^{o}C. They found that the addition of K_2CO_3 and Na_2CO_3 enhanced the production of phenols with methoxy groups, while NaOH and KOH enhanced the production of phenols with no methoxy groups (estimated to represent 80 wt.% of GC/MS total peak area).

Based on literature reports, there are limited studies comparing the catalytic pyrolysis of industrial lignins from three different types of biomass (hardwood, softwood and non-woody) to produce phenols. In most of lignin pyrolysis studies, phenolics production was assessed based on peak area fraction, which does not give accurate estimate of the mass yields of phenols derived from the lignins; instead, a quantification using calibration standards would address this limitation [13]. In addition, most reported works on catalytic pyrolysis of lignin have adopted direct mixing of the dried powder catalyst with lignin. An alternative method to incorporate the catalysts into the lignin by impregnation, could have a more marked effect on subsequent pyrolysis, due to close contact of the catalyst with the lignin. Because of the different biomass structures of hardwood, softwood and non-woody lignins, different catalytic effects could be expected, especially with impregnated catalyst. In this work, three lignins obtained from the Kraft (eucalyptus and pine) and soda (sugarcane bagasse) processes were impregnated with KOH, NaOH, ZnO and Al_2O_3. Pyrolysis was conducted using TGA and the released volatiles were captured in thermal desorption (TD) tubes coupled to the TGA. The TD tubes were desorbed into the gas chromatography-mass spectrometry (GC-MS), and the phenols yields were quantified by internal calibration. Catalyst amount equivalent to 1% of the lignin mass was selected in order to investigate potential catalytic effect on primary mechanisms, based on modifications of thermogravimetric curves and phenols yields.

5.2. Materials and methods

5.2.1. Materials

The three lignin samples investigated in this study were purified soda sugarcane bagasse lignin, and two Kraft (*eucalyptus grandis* and pine) lignins recovered from black liquors received from the South African pulping industries. Acid purification was done by acidifying them to a pH of 2 with sulphuric acid at a concentration of 98%, as described in our earlier work [14]. The three lignins bear the following abbreviated names: soda sugarcane bagasse lignin (S-S), Kraft eucalyptus lignin (E-K), and Kraft pine lignin (P-K). The characteristics of the purified lignins (proximate and ultimate analyses) are presented in Table 5-1. The details of how the isolation, purification and characterisation were done can found in our earlier work [14]. The catalysts: Al_2O_3 purchased from Fizmerk, NaOH purchased from ScienceWorld, ZnO and KOH purchased from Edutrade, all of analytical grade with purity of about 98%, were used for the catalytic pyrolysis of the three lignins. Standards of analytical grades (purity ≥98%) purchased from Sigma-Aldrich were used for GC/MS calibration. They include 4-ethylguaiacol, 4-vinylguaiacol, eugenol, syringol, 4-methylsyringol, allylsyringol, acetosyringone, guaiacol, creosol, 4-propylguaiacol, trans-isoeugenol, isoeugenol, vanillin, acetoguaiacone, 3-methoxycatechol, 3-hydroxy-4-methoxyacetophenone, phenol, o-cresol, 2,6-dimethylphenol, p+m cresol, 2,4-xylenol, catechol, 4-ethylphenol, anisole, 4-methylanisole, ethenylanisole, toluene and furfural.

5.2.2. Methods

5.2.2.1. Lignin impregnation with catalyst

Prior to catalytic pyrolysis experiments, the lignins were impregnated with an amount of the catalyst corresponding to 1 wt.% of each lignin mass using a method adapted from Collard et al. [15], and Wang et al. [16]. Impregnation was ensured by the addition of 20 mL of distilled water to the mixture of each lignin sample (2 g) and catalyst placed in a 150 mL Schott bottle. The solutions were stirred on a Velp Scientifica multiple stirring system set at 300 rpm at room temperature for 24 h. Thereafter, the solutions were heated to 80 ^{o}C on a magnetic stirring hotplate set at 100 rpm to evaporate the water until slurries of the solutions leading to resistive movement of the magnet was attained. Samples were then dried in the oven at 100 ^{o}C for 24 h. The dried samples were reduced to particle sizes of ≤ 425 µm and then packed in air-tied bags prior to pyrolysis experiments.

5.2.2.2. Catalytic Pyrolysis by TGA-TD-GC/MS

Pyrolysis was conducted using a recently developed method referred as TGA-TD-GC/MS [14,17]. A thermogravimetric analyser (Mettler Toledo TGA/DSC 1-LF1100) system was employed to pyrolyse the lignin samples. The evolved pyrolytic volatiles were captured into stainless-steel thermal desorption (TD) tube coupled to the TGA. The TD tube is industry-standard sized with ¼ inch outer diameter and 3½ inch long model C1-AAXX-5003, conditioned and capped from MARKES International, UK. The sorbent tube material was Tenax TA with adsorption capacity for volatile compounds ranging from n-$C_{6/7}$ to about n-C_{30} with a temperature limit of 280-320 ^{o}C for analysis and 330 ^{o}C for conditioning. About 10 mg of each lignin was loaded into a 600 µL crucible, and placed into the furnace aided by a robot, and then heated from

30 ºC to 600 ºC at a heating rate of 10 ºC/ min. Argon (baseline 5.0 Afrox) flowing at the rate of 70 mL/min was used as carrier gas. 3 µL of 2-octanol (6.1 g/L) used as internal standard was injected into the TD tube prior to desorption. The TD tube was desorbed into an Agilent Technology 7890A GC through a thermal desorption (Unity 2) system, heated to 320 ºC for 10 min. Volatiles removal from the TD tubes, and transfer into the GC-MS line was aided by helium gas flowing at the rate of 10 mL/min and a split flow of 30 mL/min. The GC was coupled to an Agilent Technologies 5975C MS for the quantification of the volatiles. The GC was equipped with 14% cyanopropylphenyl-methylpolysiloxane capillary column (ZB-1701, 60 m x 0.25 mm x 0.25 µm-Agilent Technologies). The temperature of the GC oven was programmed from 45 ºC (isothermal 10 min) to 100 ºC with a heating rate of 2 ºC/min and then to 260 ºC (14 min) with a heating rate of 7 ºC/min. The mass spectrometer was operated in EI mode at 70 eV. The detected mass-to-charge (m/z) ratio ranged from 20 to 500. 29 standard compounds prepared at 5 known concentrations were injected into the GC-MS for phenols calibration. An ACS grade acetone (>99.9% pure from Sigma Aldrich) was used to carry out the dilutions of the standard compounds. Calibration curves were prepared by the injection of 3 µL of the standard solution and 3 µL of internal standard following the same TD-GC-MS method. For compound identification, NIST 2011 mass spectrometer library was used, together with the comparison of the retention times of the compounds with those of the standard compounds. All experiments were conducted at least two times to confirm the reproducibility and accuracy of the data. The acceptable variability associated with the total phenols yield for one couple (lignin/catalyst) was when the relative standard deviations (RSD) was < 25%. A student's t-test (two samples assuming equal

variance) was used to assess whether there was a significant difference between the yields generated with and without catalyst.

5.3. Results and discussion

5.3.1. Characterisation of lignin samples

The results from the proximate and ultimate analyses of the three lignins are presented in Table 5-1. From the proximate analysis, the P-K lignin had a lower amount of volatile matter (63.0%), and a higher of fixed carbon (36.8%) than those of S-S and E-K lignins (66.7% and 65.9%) and (29.6% and 34.8%) respectively. P-K is a softwood lignin, which is more thermally stable, and hence, released less volatiles during pyrolysis than hardwood and herbaceous lignins [18]. The ash content of S-S lignin was higher (4.5%) than for E-K and P-K lignins (0.9% and 1.2 %) respectively, which was ascribed to its origin (herbaceous plant), known to contain more silicate than woody lignins [14,19]. The residual sugars present in the lignins were 6.4 wt.% for S-S lignin, 0.4 wt.% for E-K lignin, and 0.6 wt.% for P-K lignin. The higher residual sugar content for S-S lignin than for E-K and P-K lignin was ascribed to an incomplete separation of the lignin-carbohydrate complexes (LCC) [20]. The characteristics of the three lignins are within the range reported in literature [21,22].

Table 5-2: Proximate analysis, elemental and sugar contents of three lignins

	Proximate analysis (wt.% dry basis)			Elemental content (wt.% dry basis)				
Lignin Name	Volatile Matter	Fixed Carbon	Ash	C	H	N	S	Total sugars (wt.% dry basis)
S-S	66.7	29.6	4.5	61.2	5.5	0.2	4.6	6.4
E-K	65.9	34.8	0.9	62.9	5.6	0.2	4.6	0.4
P-K	63	36.8	1.2	64.6	6.3	0.6	6.3	0.6

5.3.2. Pyrolysis behaviours of the lignin types

Pyrolysis of the three lignins with and without catalysts were conducted using thermogravimetric analyser (TGA) from ambient temperature to 600 ^{o}C, and the thermogravimetric (TG) curves which indicate the mass loss of the various lignin samples in relation to the temperature are presented as supplementary Figure S5-1. The differential TG curves (DTG) which reveal the corresponding rate of mass losses are shown in Figure 5-1a-d. Almost all the DTG curves for the three lignin types pyrolysed with and without catalyst showed two main decomposition peaks. Table 5-2 presents the summary of the first and second peak temperatures of the DTG curves, and the char yields produced at the end of pyrolysis. The first DTG peaks were observed with a maximum intensity at temperature between 237 and 331 °C, while the second DTG peak which generally corresponded to the temperatures of maximum degradation rates (DTG_{max}), were between 349 and 391 °C.

Differences in lignin properties affected the pyrolysis thereof in the absence of catalyst. From Figure 5-1a for the pyrolysis without catalyst, the first decomposition peaks appeared at 272 ^{o}C, 247 ^{o}C and 250 ^{o}C for S-S, E-K and P-K lignins respectively. Literature on lignocellulose pyrolysis, within these temperatures usually assigned the peak appearances to hemicelluloses decomposition [19]. However, the mass losses corresponding to the first peaks were 15 wt., 9 wt.%, and 12 wt.% for S-S, E-K, and P-K lignins respectively (Figure S5-1a), which were higher than the sugar contents of the respective lignins (Table 5-1). Hence, together with hemicellulose decomposition, these mass losses were also due to the degradation of the less stable chemical groups present in lignin, which are known to decompose within similar temperature regions. For example, the cleavage of some ether bonds, in particular β-O-4, have been reported in the temperature range of 250-350 ^{o}C [23]. The intensity of

the first main peak of S-S lignin was higher than those of E-K and P-K lignins, which could be attributed to the contribution of its higher sugar content (Table 5-1). The second decomposition stage, which corresponded to the maximum decomposition rates (DTG_{max}) of lignin, had peak temperatures located at 376 ºC, 373 ºC and 390 ºC for S-S, E-K and P-K lignins respectively. The differences in the maximum decomposition temperatures were ascribed to the differences in the thermal stability of the lignins. The phenylpropane units of herbaceous (S-S) and hardwood (E-K) lignins are mostly linked by ether bonds [19,24], which are easier to break than the mostly condensed C-C bonds [24], inherent in the structure of softwood (P-K) lignin. The increased thermal stability of softwood lignin compared to hardwood and herbaceous lignins has been reported before [18,23].

With regards to char generated for the pyrolysis without catalyst (Table 5-2), P-K lignin produced more char (41.0 wt.%) than S-S (35.9 wt.%) and E-K (39.1 wt.%) lignins, consistent with the respective ratios of fixed carbon/volatile matter (Table 5-1). Furthermore, literature has shown that lignin with relatively low methoxyl group content, which is typical of softwoods [25], is more thermally stable, and causes the formation of more char during pyrolysis than lignins with higher content of methoxyl groups [26,27], hence, the higher char yield for P-K than for S-S and E-K lignins.

Based on the catalytic pyrolysis DTG curves (Figure 5-1b-d), a catalytic effect impacting some primary mechanisms was observed. For S-S lignin (Figure 5-1b), a clear catalytic effect was observed with the hydroxide catalysts, while the profiles observed with the oxide catalysts were similar to that of the conversion without catalyst. Regarding the first decomposition stage, the peak maximum was observed at 271.9 °C without catalyst and was followed by a mass loss rate decrease up to 300 ºC (Table 5-2). In presence of hydroxides, the mass loss rate kept increasing up to 307.1

and 331.4 °C with KOH and NaOH respectively. At the end of the first degradation stage, the mass loss with KOH was approximately 21% against 11-15% for the conversion without catalyst or with oxide catalysts. Therefore, KOH promoted the cleavage of some bonds, resulting in the production of more volatiles in the first decomposition stage than with other catalysts. With NaOH, the mass loss corresponding to the first decomposition stage could not be determined due to an overlap with the peak of the second stage. The DTG_{max} for catalytic pyrolysis of S-S lignin had peaks at 377 ^{o}C for Al_2O_3 and 372 ^{o}C for both ZnO and KOH. The intensities of the second peaks were observed to be slightly lower than without catalyst. This result could be due to the recombination of some volatiles at the surface of the catalyst, leading to the formation of secondary char [28]. In the case of NaOH, the two decomposition stages had their maxima at close temperatures, resulting in a broad peak between 331-349 ^{o}C. Broad DTG peak appearance during lignin pyrolysis has been associated with the inhibition of volatilisation [29], meaning that despite a positive effect on the first decomposition stage, NaOH was not more effective with the conversion of S-S lignin than other catalysts. The yields of char residues (36.2-39.9 wt%) generated from the catalytic pyrolysis of S-S lignin were higher than the one obtained without catalyst (35.9 wt.%). Several literature reports have shown that pyrolysis of lignin with additives such as KCl, NiO, Fe_2O_3 and TiO_2 (Aeroxide) promoted char formations [10,11,28]. This phenomenon can be due to the effect of impregnated catalyst which can enhance rearrangement reactions within lignin matrix (primary reaction) [15] and/or the formation of secondary char due to recombination of volatiles at the surface of the catalyst [8]. The char yield with KOH (36.2 wt.%) was found to be much lower than with the other catalyst, confirming the higher influence of KOH on the depolymerisation of S-S lignin.

For the catalytic pyrolysis of E-K lignin, the DTG curves showed two main decomposition peaks (Figure 5-2c). The first decomposition peaks appeared between 238-243 ^{o}C and had peak intensities that resembled that obtained without catalyst. The masses losses in this range were about 5-7 %, much higher than the sugar content of E-K lignin (0.4 wt.%). Therefore, the first peak was mostly ascribed to lignin decomposition. The second mass loss peaks corresponding to the maximum degradation rates were within the range of 358-374 ^{o}C (Figure 5-1c-d). Compared to the DTG_{max} of the non-catalysed pyrolysis (373 ^{o}C), the two hydroxides reduced the maximum degradation temperatures (358 ^{o}C and 367 ^{o}C) more substantially than the metal oxides (372 ^{o}C and 374 ^{o}C), with an effect more pronounced for NaOH (358 ^{o}C). Another particularity with NaOH was the higher intensity of the DTG curve between the first peak and 300 °C, probably due to a catalytic effect enhancing the production of volatiles at relatively low temperature. The temperature reductive power of NaOH has been reported in literature, as partly due to its ability to enhance swelling during impregnation, probably due to intimate contact of the Na+ with the biomass material [16]. In terms of char residues generated from catalytic pyrolysis of E-K, as with S-S lignin, the char residues were higher (41-43 wt.%) than without catalysts (39 wt.%), meaning that the catalysts promoted char formation.

For P-K lignin catalytic pyrolysis (Figure 5-1d), the first decomposition mass loss was observed at peak temperatures between 240-249 ^{o}C. The mass losses associated with the first peaks were 8-9%, which showed that together with polysaccharides (sugar content of 0.6 wt.%) the lignin component started to get degraded. Between the two peaks (250-320 °C), the intensities of the DTG signals for the two hydroxides were higher than those observed for the metal oxides. This was ascribed to a more pronounced catalytic role of NaOH and KOH at this temperature range. The DTG_{max}

was also observed to be lower for NaOH and KOH (378 ^{o}C and 380 ^{o}C) respectively, than those of the metal oxides (390-391 ^{o}C), as compared to the DTG_{max} for the pyrolysis without catalyst (390 ^{o}C). Hence, like the trends for S-S and E-K lignins (Figure 5-1b-c), the two hydroxide catalysts enhanced devolatilisation at lower temperatures than the metal oxides. Regarding the char residues from the P-K lignin, the presence of catalyst resulted in increased char yields (Table 5-1), similarly to what was observed with the S-S, and E-K lignins (Table 5-2). The differences in char yields depending on the catalyst type, were less pronounced than with those of the S-S and E-K lignins.

Overall, for the three lignin types, it was observed from the DTG profiles that the hydroxide catalysts had more influence on the modification of the conversion mechanisms than the oxide catalysts (Figure 5-1b-d), especially with the sugarcane lignin (Figure 5-1b). The main effect was an increase in mass loss rate at a relatively low temperature. However, char yields with the different catalysts were found to be higher than without catalysts (Table 5-2).

Table 5-2: Temperatures of the first and second peaks of the DTG curves and char yields of S-S, E-K, and P-K lignins

First dTG peaks (ºC)					
	No Catalyst	Al_2O_3	ZnO	NaOH	KOH
S-S	271.9	255.3	281.5	331.4	307.1
E-K	247.1	242.3	243	237.5	237.6
P-K	249.7	247.6	245.4	248.7	245.4
Second dTG peaks (ºC)					
	No Catalyst	Al_2O_3	ZnO	NaOH	KOH
S-S	376.1	376.5	371.8	348.9	371.7
E-K	373.1	374.2	372.2	358.4	366.6
P-K	390.1	391	389.9	378.3	379.5
Char Yield (wt.% dry, ash, catalyst-free basis)					
	No Catalyst	Al_2O_3	ZnO	NaOH	KOH
S-S	35.9	39.9	39.4	39.4	36.2
E-K	39	41	42.3	42.9	42
P-K	41.9	43.7	43.6	44.4	43

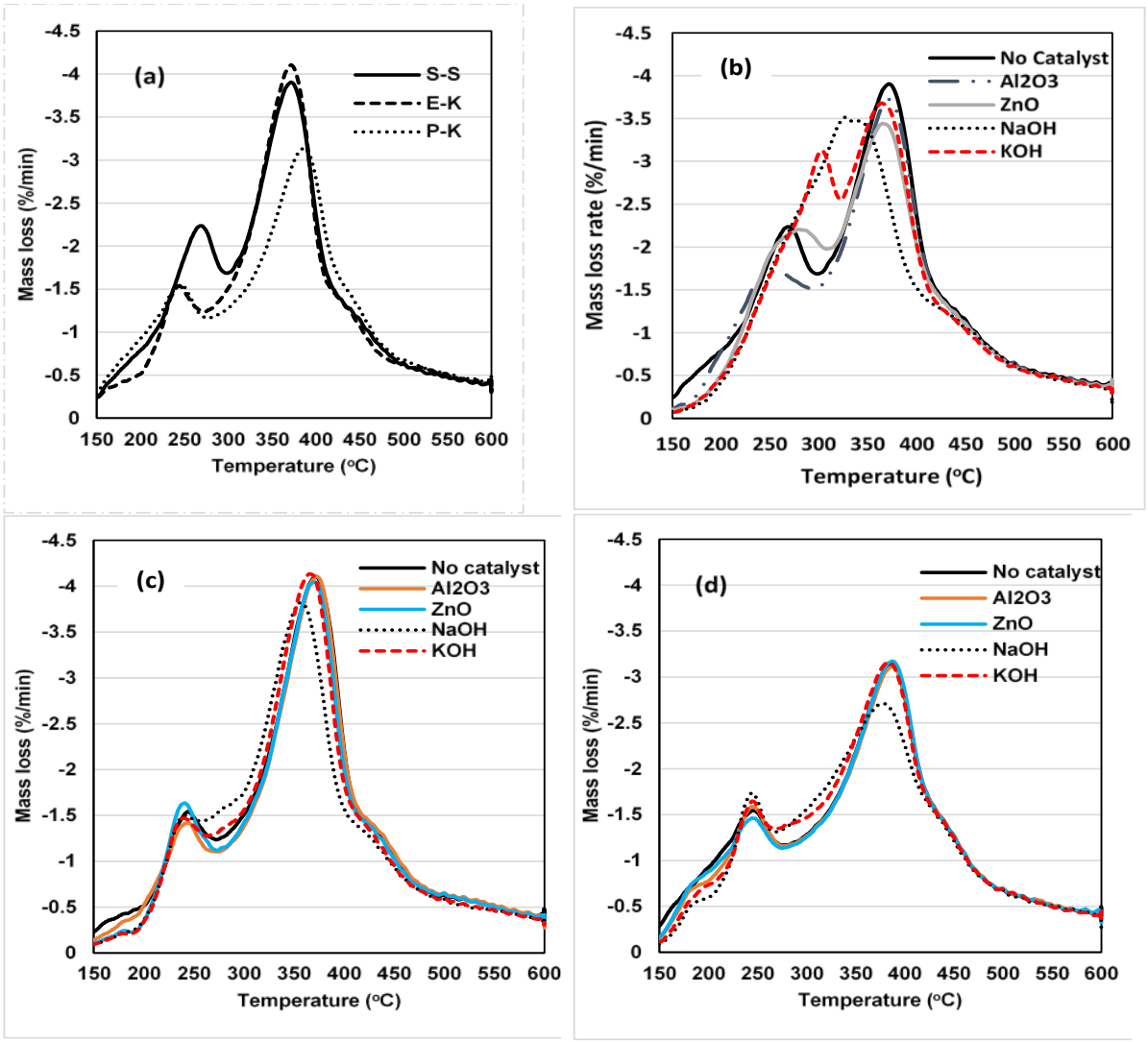

Figure 5-6a-d. First derivative thermogravimetric (DTG) curves of the pyrolysis of sugarcane (S-S), Eucalyptus (E-K), and pine (P-K) lignins without catalysts (a), and with catalysts (b) for S-S, (c) for E-K, and (d) for P-K lignins.

5.3.3. Phenols products yields

The volatiles released from the TGA pyrolysis, and captured in TD tubes, were quantified using GC/MS. A total of 29 compounds were quantified, out of which 27 were phenolic compounds. The phenolic compounds produced were classified into three types of phenols namely, syringol-type (S-type) phenols, guaiacol-type (G-type) phenols, and phenol-type (P-type) phenols, based on the number of methoxy groups on the benzene

ring, as presented in Tables 5-3, 5-4, and 5-5 for S-S, E-K, and P-K lignins respectively. Figure 5-2 illustrates the various changes in total phenols yields from the catalytic pyrolysis, while Figure 5-3a-c shows the yields of the three groups of phenols, determined by the sum of the yield of the phenolic compounds under each group. Only phenolic compounds obtained in amounts exceeding 0.03 wt.% were included.

5.3.3.1. Effect of catalyst on the yield of total phenols

As earlier stated, (section 5.2.1.2), lignin was pyrolysed with and without catalysts in at least duplicate experiments, and the total yields of phenols were calculated. The average relative standard deviation (RSD) of the total yields of phenols was less than 12% for the three lignin types. From Tables 5-3-5, considering S-S lignin, the non-catalytic pyrolysis generated 9.0 ± 2.1 wt.% total phenols. With the catalysts Al_2O_3, ZnO, and KOH, despite the increased char yield (Table 5-2), the total phenols yields were also increased to 10.0 ± 2.4 wt.%, 10.6 ± 2.5 wt.% and 11.3 ± 2.7 wt.% (p-values of 0.32, 0.22 and 0.15), corresponding to 11.1%,17.8%, and 25. 6% increases respectively (Figure 5-2). The performance of KOH with S-S lignin is consistent with the relatively low char yield observed. Based on the DTG curve, the higher phenols yields could be correlated to a very strong peak at around 307 ^{o}C in the first decomposition stage (Figure 5-1b). With NaOH, the yield of total phenols decreased by 12%. This behaviour is consistent with its DTG curve (Figure 5-1b), where an inhibition of the depolymerisation reactions during the second degradation stage was observed [29].

For E-K lignin, the non-catalytic pyrolysis produced 4.3 ± 0.3 wt.% of total phenols. With catalytic pyrolysis, all the catalysts (Al_2O_3, ZnO, NaOH, and KOH) increased the yields of total phenols to 4.6 ± 0.3 wt.%, 4.5 ± 0.3 wt.%, 6.0 ± 0.4 wt.%, and 5.0 ±

0.4 wt.%, respectively. These yields differed from that obtained without catalyst with increases of approximately 7.0%, 4.7%, 40.0%, and 16.3% respectively. The yields differences obtained with NaOH and KOH were found to be statistically significant (p-values = 0.04 and 0.09) respectively, while those obtained with Al_2O_3 and ZnO were not statistically significant (p-values = 0.19 and 0.35) respectively. The highest yield increase (40%) obtained with NaOH, was attributed to the higher intensity of the DTG signal between the first peak and 300 °C (Figure 5-3b).

With the P-K lignin, the pyrolysis without catalyst generated 5.6 ± 0.2 wt.% of total phenols. When pyrolysed with the various catalysts, only NaOH was found to increase the yield to 6.0 +/- 0.2 wt.% (p-value = 0.12). The performance of the various catalysts with the P-K (softwood) lignin was quite weak, in comparison with the E-K (hardwood) and S-S (herbaceous) lignins. It is well known that the phenylpropane structures of softwood lignin are linked mostly by condensed (C-C) bonds, and a much lower number of ether bonds, in particular (β-O-4) bonds [24]. Due to the electrophilic nature of metal atoms, it has been suggested that interactions of metal catalysts in biomass could be mostly with the oxygen elements [15], thus the limited catalytic effect on the linkages between the units of softwood lignin.

Overall, in terms of total yields of phenols, the more pronounced catalytic effects were obtained with the hydroxide catalysts (Table 5-3-5). This was probably due to more intimate contact between the nucleophilic oxygen atoms present in lignin and the metal cations (released during impregnation with hydroxides) than with the metals in form of metal oxides [15,16].

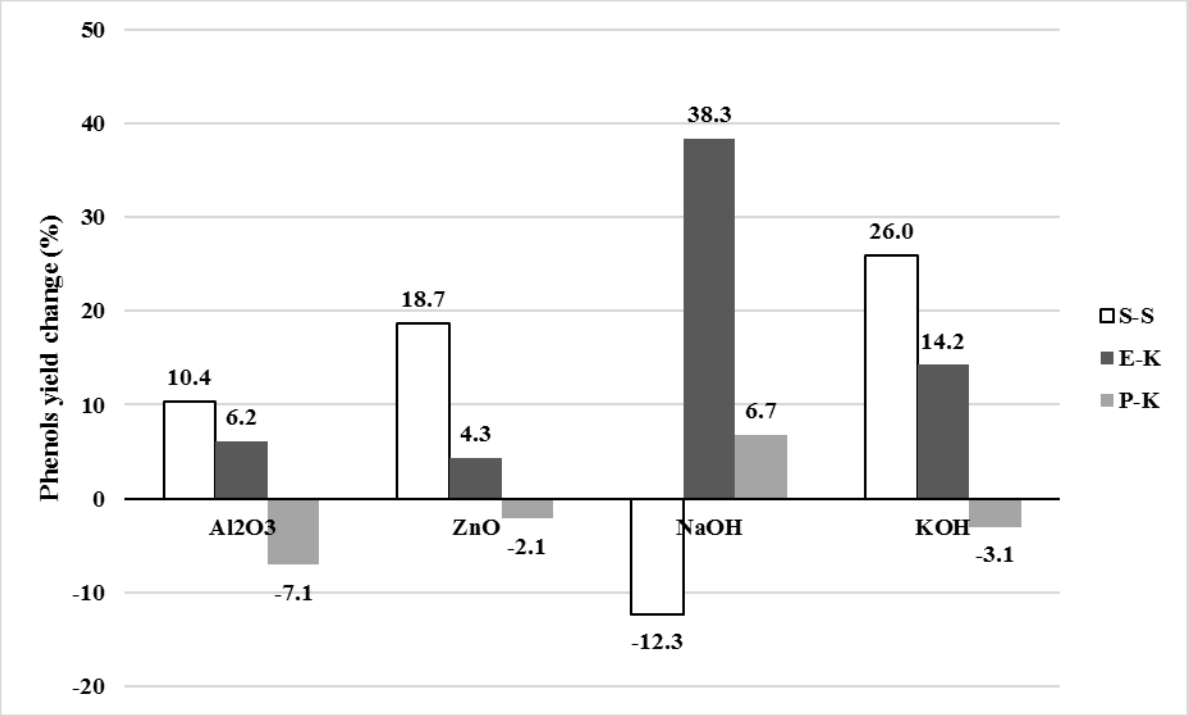

Figure 5-2. Phenols yields change (%) obtained from catalytic pyrolysis of S-S, E-K, and P-K lignins.

5.3.3.2. Effect of catalyst on the yields of specific phenolic compounds

The distribution of phenolic products was categorised into syringol (S)-type, guaiacol (G)-type and phenol (P)-type groups, as illustrated in Figure 5-3a-c. For S-S lignin (Figure 5-3a), KOH was clearly the best performing catalyst with significant increases of the production of G-type (+32%) and S-type (+34%) phenols. The main S-type compound obtained from S-S lignin, was syringol, of which KOH significantly improved the yield from 0.7 wt.% to 1.0 wt.%, equivalent to 43% increase. For the G-type phenols, KOH increased the yields of guaiacol and 4-vinylguaiacol by 32% and 40% respectively. Vinylguaiacol yield reached 2.80 wt.%, which is high compared to typical yields of 0.6-0.9 wt.% reported in literature [9]. Nair and Vinu [11] reported higher yield increases of these two compounds (+106% and +62%) with TiO_2 catalyst, but catalyst content was 10 times higher than in this work. Generally, the production of S-type and G-type phenolic compounds is favoured by low temperature

pyrolysis [30]. It has been reported that the methoxyl groups of S- and G-type units are degraded quickly at temperatures higher than 350 °C [31]. Therefore, the selectivity of KOH towards the production of the S-type and G-type compounds correlated with the substantial increase in the intensity of the first DTG peak (Figure 5-1b). Regarding the effect of the oxides Al_2O_3 and ZnO, while the change on the yields of S- and G-type phenols was less evident, an increase in the yields of H-type equivalent to 29% and 36%, (p-value = 0.11 and 0.10) respectively, as compared to the non-catalytic yield (Figure 5-3a) was observed. The main P-type phenols obtained in significant amounts were phenol, o-cresol and ethylphenol of which ZnO produced the highest change, resulting in increases up to 39%, 32% and 54% respectively (Table 5-3). The production of the P-type phenols indicated that demethoxylation reaction of the S-type and G-type phenols was enhanced [32]. With NaOH, due to the inhibition of the depolymerisation reactions during the second degradation stage, the yields of the different types of phenols decreased.

For E-K lignin, the presence of the oxides had very little influence on the distribution of the phenolic products. The yields of S-type phenols obtained with NaOH and KOH were found to increase by 51% and 22%, with significant statistical effect (p-values of 0.01 and 0.03) respectively. As with the S-S lignin, syringol was the major S-type phenolic compound produced. With NaOH and KOH, its production increased by 90%, and 37% respectively. The relatively high yield of syringol (1.9 wt.%), as compared to the non-catalytic yield (1.0 wt.%), demonstrates the effectiveness of NaOH for the production of such compound with hardwood lignin. For the G-type phenols, the hydroxide NaOH and KOH increased the yields by 30% and 10% respectively, with significant effects for both catalysts (p-values = 0.09 and 0.07). The production of 3-methoxycatechol from E-K (hardwood) lignin is consistent with

literature [18,32], whose mechanism of formation involves demethylation of syringol derivatives [18]. With NaOH, the yields of guaiacol and 3-methoxycatechol increased by about 79% and 29% respectively, while increases of about 31% and 25% respectively, were observed with KOH.

For the catalytic pyrolysis of P-K lignin, as expected with softwood lignin, majority of the products were the guaiacol-type phenols followed by the P-type phenols (Figure 5-3c). The yield of G-type phenols was not increased by more than 16% (with NaOH), and the effect was found to be not statistically significant (p-values > 0.25). This is an indication that the catalysts had minimal influence on the production of G-type phenols from P-K (softwood) lignin. However, the yield of guaiacol as the main G-type compound was improved by NaOH (41% increase with p-value of 0.003). For the P-type phenols, only the yield increase obtained with ZnO (22%) as compared to the non-catalytic yield was found to be almost significant (p-value of 0.12). The production of catechol, the major P-type phenols, increased by 85% with ZnO. The formation of catechol signifies that substitution of the methoxyl group by an hydroxide on the G-type units was enhanced by ZnO from P-K lignin [33].

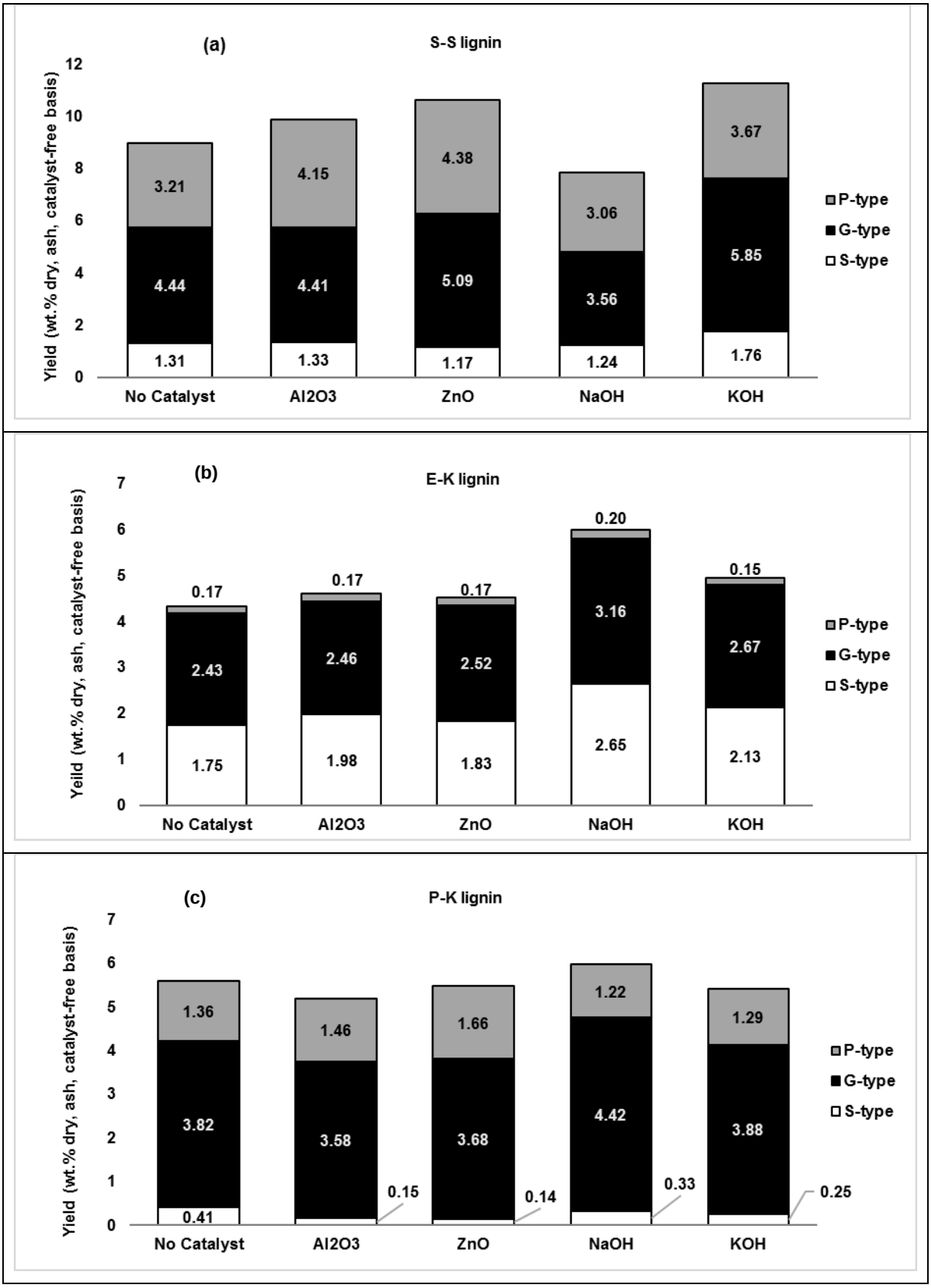

Figure 5-3a-c. Yields of S-type, G-type, and P-type phenols from catalytic pyrolysis of S-S lignin (a), E-K lignin (b), and P-K lignin (c).

Table 5-3: Yields of monomeric products (wt.% dry, ash, catalyst-free basis) from catalytic pyrolysis of S-S lignin

Compound	No Catalyst	Al_2O_3	ZnO	NaOH	KOH
Syringol-type					
Syringol	0.68	0.70	0.64	0.87	0.96
4-methylsyringol	0.47	0.47	0.43	0.24	0.58
Acetosyringone	0.16	0.16	0.11	0.13	0.22
Sum	**1.31**	**1.33**	**1.17**	**1.24**	**1.76**
Guaiacol-type					
Anisole	0.14	0.21	0.03	0.16	0.10
4-methylanisole	0.12	0.16	0.18	0.13	0.13
Guaiacol	1.06	1.29	1.24	0.55	1.40
creosol	0.50	0.59	0.58	0.29	0.59
4-ethylguaiacol	0.23	0.38	0.35	0.25	0.32
4-vinylguaiacol	2.01	1.40	2.29	1.79	2.80
Isoeugenol	0.22	0.21	0.23	0.24	0.28
Vanillin	0.08	0.08	0.11	0.07	0.12
Acetoguaiacone	0.08	0.09	0.08	0.07	0.11
Sum	**4.44**	**4.41**	**5.09**	**3.56**	**5.85**
Phenol-type					
Phenol	1.28	1.66	1.79	1.44	1.54
o-cresol	0.75	0.94	0.99	0.75	0.83
p+m-cresol	0.73	0.90	0.94	0.50	0.78
2,4-xylenol	0.11	0.13	0.15	0.09	0.12
4-ethylphenol	0.34	0.52	0.52	0.28	0.40
Sum	**3.21**	**4.15**	**4.38**	**3.06**	**3.67**
Others					
Toluene	0.29	0.33	0.35	0.30	0.32
Furfural	1.88	4.55	2.44	0.43	1.57
Total phenols yield	**8.96**	**9.89**	**10.64**	**7.86**	**11.29**

Table 5-3: Yields of monomeric products (wt.% dry, ash, catalyst-free basis) from catalytic pyrolysis of E-K lignin

Compound	No Catalyst	Al_2O_3	ZnO	NaOH	KOH
Syringol-type					
Syringol	0.98	1.08	1.02	1.86	1.34
4-methylsyringol	0.62	0.73	0.64	0.60	0.62
Acetosyringone	0.15	0.17	0.17	0.18	0.17
Sum	**1.75**	**1.98**	**1.83**	**2.65**	**2.13**
Guaiacol-type					
Guaiacol	0.61	0.66	0.62	1.09	0.80
creosol	0.32	0.34	0.33	0.32	0.31
4-ethylguaiacol	0.13	0.14	0.14	0.16	0.15
4-vinylguaiacol	0.44	0.33	0.36	0.47	0.37
3-methoxycatechol	0.57	0.66	0.74	0.73	0.71
Isoeugenol	0.25	0.23	0.24	0.26	0.24
Vanillin	0.04	0.02	0.04	0.05	0.04
Acetoguaiacone	0.07	0.07	0.07	0.07	0.06
Sum	**2.43**	**2.46**	**2.52**	**3.16**	**2.67**
Phenol-type					
Phenol	0.11	0.11	0.11	0.13	0.11
p+m-cresol	0.06	0.05	0.06	0.07	0.05
Sum	**0.17**	**0.17**	**0.17**	**0.20**	**0.15**
Others					
Toluene	0.05	0.05	0.05	0.06	0.05
Furfural	0.36	0.48	0.39	0.22	0.30
Total phenols yield	**4.34**	**4.61**	**4.53**	**6.00**	**4.96**

Table 5-4: Yields of monomeric products (wt.% dry, ash, catalyst-free basis) from catalytic pyrolysis of P-K lignin

Compound	No Catalyst	Al_2O_3	ZnO	NaOH	KOH
Syringol-type					
Syringol	0.22	0.06	0.05	0.18	0.12
4-methylsyringol	0.16	0.07	0.06	0.12	0.10
Acetosyringone	0.04	0.03	0.02	0.03	0.03
Sum	**0.41**	**0.15**	**0.14**	**0.33**	**0.25**
Guaiacol-type					
Guaiacol	1.37	1.21	1.28	1.93	1.38
creosol	0.95	0.89	0.89	0.89	0.89
4-ethylguaiacol	0.24	0.24	0.25	0.27	0.24
4-vinylguaiacol	0.75	0.74	0.74	0.78	0.81
4-propylguaiacol	0.04	0.04	0.04	0.04	0.04
Isoeugenol	0.30	0.30	0.30	0.33	0.34
Vanillin	0.07	0.06	0.07	0.08	0.08
Acetoguaiacone	0.10	0.10	0.10	0.10	0.10
Sum	**3.82**	**3.58**	**3.68**	**4.42**	**3.88**
Phenol-type					
Phenol	0.27	0.24	0.26	0.25	0.23
o-cresol	0.33	0.29	0.30	0.28	0.27
p+m-cresol	0.23	0.22	0.23	0.19	0.19
2,4-xylenol	0.06	0.06	0.06	0.05	0.05
4-ethylphenol	0.06	0.04	0.04	0.04	0.04
Catechol	0.41	0.61	0.76	0.41	0.50
Sum	**1.36**	**1.46**	**1.66**	**1.22**	**1.29**
Others					
Toluene	0.10	0.09	0.10	0.10	0.09
Furfural	0.19	0.06	0.14	0.09	0.12
Total phenols Yield	**5.59**	**5.20**	**5.47**	**5.97**	**5.42**

5.4. Conclusions

The catalytic pyrolysis of three lignins types namely, soda sugarcane bagasse lignin, Kraft eucalyptus lignin and Kraft pine lignin were investigated using TGA-TD-GC-

MS. In the presence of impregnated catalyst (1 wt.% content), some modifications in the primary mechanisms, in particular between 250 and 350 °C, were observed, especially with the hydroxides. The influence of the catalysts on phenols production and distribution was found to vary, depending on lignin types. While with pine catalytic effect was limited, the use of KOH increased the yields of phenols from sugarcane bagasse lignin by 26%, and likewise NaOH for eucalyptus lignins (40.0%). The production of some valuable compounds increased by up to 90% and yields of syringol (from eucalyptus) and 4-vinylguaiacol (from sugarcane) reached 1.86 and 2.80 wt.%. The production of both S-type and G-type compounds by hydroxides were probably correlated with the increased intensities of their respective DTG signals before 350 °C. With oxide catalysts, the main effect was the increase of P-type phenols due to the enhancement of demethoxylation reaction.

Conflict of interest

We have no conflict of interest regarding this project

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CHAPTER SIX

CATALYSTS SCREENING USING THERMOGRAVIMETRIC ANALYSIS THERMAL DESORPTION-GAS CHROMATOGRAPHY-MASS SPECTROSCOPY

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Titled: "Production of phenols from pyrolysis of sugarcane bagasse lignin: Catalyst screening using thermogravimetric analysis thermal desorption-gas chromatography-mass spectroscopy"

Authors: David Naron, Francöis-Xavier Collard, Luvuyo Tyhoda, and Johann Görgens.

Objective of dissertation and summary of findings in present chapter

This chapter addresses **objective 3**, which focussed on the screening of catalysts and sugarcane bagasse lignins for phenols production using the TGA-TD-GC-MS used in chapter 4 and 5 to achieve **objectives 1 and 2**. This was informed by the high yields of phenols obtained from the catalytic pyrolysis of sugarcane bagasse lignin compared to those of *E.grandis* and pine lignins investigated in chapter 5. The same four catalysts tested to achieve **objective 2** in chapter 5, together with eight other catalysts selected on the merits of their potential to produce phenols were screened. The repeat of the four catalysts was due to the inclusion of two additional sugarcane bagasse lignins extracted by soda-anthraquinone, and steam explosion combined with enzymatic hydrolysis processes to the soda lignin investigated in chapter 5. In addition, this was for effective comparison, given that the distribution of phenolic products varies significantly when lignins are isolated from the same biomass origin by different methods. In total, twelve catalysts namely CaO, NiO, Al_2O_3, Ni/Al_2O_3-SiO_2, Fe_2O_3, MoO_3, TiO_2, ZnO, MgO, CuO, KOH and NaOH were each impregnated into three sugarcane bagasse lignins with amounts equivalent to 1 wt.% of the lignin mass, to

evaluate the catalysts abilities to increase the yields and selectivities to phenolic products from each of the lignins. This was achieved by pyrolysing each impregnated lignin at 600 ^{o}C using a heating rate of 10 ^{o}C/min, similar to the pyrolysis conditions used to achieve **objective 2**.

The results showed that the performances of the catalysts depended on the lignin types of which KOH produced the most effects, leading to the highest yield increase of total phenols from soda (SD) lignin (11.2 wt.%), equivalent to +25.7% increase, and likewise CaO, from soda-anthraquinone (SAQ) lignin (8.2 wt.%), equivalent to +59.7% increase, and Fe_2O_3 from steam explosion combined with enzymatic hydrolysis (SEH) lignin (8.6 wt.%), equivalent to +43% increase. The yields of some specific phenolic compounds namely, syringol, guaiacol, and 4-vinylguaiacol were remarkably increased up to 121%, 93%, and 84% from SAQ lignin respectively, demonstrating the effectiveness of impregnation method given the low catalyst content (1 wt.%) used when compared to the ≥ 10 wt.% reported in literature. Following the performance of KOH with the soda (SD) lignin, leading to high yields of phenols, a further investigation was ensued to achieve **object 4** in chapter 7.

Candidates Declaration

With regards to chapter 6, page numbers 173 to 214 of this dissertation, the nature and scope of my contribution were as follows.

Nature of contribution	**Extent of contribution (%)**
Planning of the experiments	70
Execution of the experiments	100
Interpretation of the results	60
Writing the chapter	100

The following co-authors have contributed to Chapter 6 pages numbers 173 to 214 of this dissertation as follows:

Name	e-mail address	Nature of contribution	Extent of contribution (%)
François-Xavier Collard	fcollard@sun.ac.za	Planning of the experiments	30
		Reviewing the chapter	40
		Interpretation of results to correlate with literature	20
Luvuyo Tyhoda	ltyhoda@sun.ac.za	Reviewing the chapter	30
		Interpretation of results to correlate with literature	10
Johann F. Görgens	fgorgen@sun.ac.za	Reviewing the chapter	30
		Interpretation of results to correlate with literature	10

Signature of candidate…….

Date…….

Declaration by co-authors

The undersigned hereby confirm that the declaration above accurately reflects the nature and extent of contributions of the candidates and co-authors to chapter 6 pages number 173 to 214

in the dissertation no other authors contributed to chapter 6 pages number 173 to 214 in the dissertation besides those specified above, and potential conflicts of interest have been revealed to all interested parties and that are necessary arrangements have been made to use the material in to chapter 6, page numbers 173 to 214 of this dissertation.

Signature	Institutional affiliation	Date

Abstract

The structural nature of lignin renders it suitable as a renewable source of phenolic compounds. The production of phenols from pyrolysis of sugarcane lignins with impregnated catalysts was investigated by screening of twelve catalysts (Al_2O_3, CaO, Fe_2O_3, TiO_2, ZnO, MgO, CuO, MoO_3, NiO, Ni/Al_2O_3-SiO_2, NaOH, and KOH) at 1 wt.% content. Sugarcane bagasse lignins were isolated after soda-pulping (SD), soda-anthraquinone-pulping (SAQ) and steam explosion pre-treatment followed by enzymatic hydrolysis (SEH). Pyrolysis was conducted using a thermogravimetric analyser (TGA), and captured volatiles were quantified by thermal desorption (TD) gas chromatography-mass spectroscopy (GC-MS). The TGA results showed that the degradation profiles and char yields were influenced by the presence of catalysts, through modifications in conversion mechanisms. The highest increases in the total yield of phenols were obtained with KOH for SD lignin (+ 25.7%), CaO for SAQ lignin (+ 59.7%), and Fe_2O_3 for SEH lignin (+ 43.0%). Due to the enhancement of depolymerisation at low temperature (< 350 ^oC), the yields of syringol, guaiacol, and vinylguaiacol increased by 41%, 32%, and 43% for SD lignin, 121%, 93%, and 84% for SAQ lignin, and 72%, 77%, and 54% for SEH lignin respectively. These significant increases in the yields of phenols using 1 wt.% compared to ≥ 10 wt.% reported in literatures demonstrated the effectiveness of impregnation method.

Key Words: Lignin, Catalytic pyrolysis, TGA, TD-GC-MS, Phenols

6.1. Introduction

Lignin is one of the three major constituents of lignocellulosic biomass and represents about 15-40 wt.% of the lignocellulosic feedstock depending on the plant species by dry weight [1,2]. Lignin is generated as a by-product by the lignocellulose-pulping industry (i.e. soda-, soda-anthraquinone-, Kraft-pulping etc.), and the emerging

cellulosic ethanol processes (i.e. steam explosion pre-treatment followed by enzymatic hydrolysis). Most of the industrial lignin residues are burnt to generate power and/or recover pulping chemicals [3,4]. However, the lignin phenolic structure renders it suitable as a potential renewable source of phenolic marketable chemicals, which are currently derived from petrochemical aromatic hydrocarbons [5]. Phenolic compounds are widely used in various applications such as platform chemicals in the fields of adhesives, cosmetics, specialty polymers, food aromas, pesticides, pharmaceuticals, resins etc. [6,7]. The US alone currently produce over 90% of its phenolic chemicals from petrochemical feedstocks extracted from non-renewable resources [8]. However, the negative impact of fossil fuels, and chemicals derived from it, on the environment have attracted global interest in the use of renewable sources of phenolic chemicals [9]. In this context, lignin appears as an alternative source that would make the future of biorefinery more promising.

To date, the conversion of lignin into value-added chemical products represents a major uncaptured opportunity in the development of a lignocellulose biorefinery [2,5]. The challenge is related to the heterogeneous chemical structure of lignin, which varies with plant species, and the extraction methods applied for its liberation from the lignocellulosic biomass [1,10]. The lignin chemical structure is made up of three monolignols known as the p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) which are phenolic C_3-units bonded by different C-O and C-C inter units. The exploitation of the underlying reaction chemistry capable of effectively breaking down these bonds, remains a challenge [11].

However, research efforts aimed at the depolymerisation of lignin for the recovery of valuable aromatic chemicals by different conversion routes, as reviewed elsewhere have intensified recently [10,12–14]. Among these efforts, pyrolysis is considered as

one of the simplest and most cost effective conversion technologies [15,16], and has recently been investigated [17–19]. Pyrolysis is a thermochemical process through which organic material is transformed in an oxygen-free environment into three primary end products, namely bio-oil, char and non-condensable gases [12,20]. The bio-oil from lignin pyrolysis is composed of a wide distribution of phenols such as guaiacol, phenol, ethylphenol, vanillin, eugenol, catechol, vinylguaiacol, syringol etc., together with oligomers composed of 2-5 monomer units, obtained through incomplete depolymerisation of the lignin polymer [21].

Phenols yields distribution depends on pyrolysis conditions and lignin composition, in particular lignin source (hardwood, softwood or non-woody) as reported elsewhere [13,22]. However, while the lignin structure is modified during its isolation, the influence of isolation method on phenols yields is scarcely documented. Zhang et al. [23] studied the correlation between the effect of isolation on the ether bonds in lignin structure and phenols yields. Using lignin cornstover isolated from three different methods, they observed that the pyrolysis of the lignin containing more ether bonds (preserved during isolation) resulted in higher phenols yield and lower char yield. Wang et al. [19] investigated the pyrolysis behaviours of pine wood lignins isolated by four different methods (alkali, Klason, organosolv and milled wood). Depending on isolation method, the extent of the modification of alkyl chains and ether linkages varied, as evidenced by FTIR and NMR analyses of functional groups distribution. Due to the higher proportion of weak ether linkages in their structures, alkali and milled wood lignins were found to produce more phenols at low temperature. In addition, higher proportion of S-type phenols were observed for these two lignin types.

The efficient recovery of these valuable chemicals present in bio-oils in low concentrations is challenging and economically unattractive [24]. Therefore, the development and application of catalytic pyrolysis processes have become imperative to further improve the yields, concentrations and selectivities of the target chemical products from lignin [5,24].

A diverse number of catalytic pyrolysis strategies have been explored, including the screening of catalysts with various types of lignin and targeting specific groups of chemical products [3,25–28]. Most of the reported catalyst screening studies were aimed at the production of hydrocarbon aromatics using zeolite catalysts [3,15,29–34], rather than the production of phenolics as considered in the present study. Generally, zeolites promote deoxygenation reactions and reduce the yields of phenolic compounds while producing hydrocarbons in the gasoline range, mostly benzene, toluene, and xylene (BTX) [15,27,35–37].

A few studies which focused on the pyrolytic production of phenols from lignins using catalysts have been reported in literature. Metal oxides and salts of alkali and alkaline earth elements have been considered as catalysts [38], as they are generally readily available and inexpensive [39]. Salts include NaOH, KOH, LiOH, $Ca(OH)_2$, K_2CO_3, $CsCO_3$, $RbCO_3$ etc., while metal oxide catalysts include Al_2O_3, Fe_2O_3, TiO_2, ZnO, CuO, MoO_3, NiO, CaO, MgO, etc. For example, Mante et al. [21] investigated the catalytic fast pyrolysis of Kraft lignin isolated from softwood using pyrolysis-gas chromatography-mass spectroscopy (Py-GC-MS), connected online to a micro catalytic reactor. The lignin was first pyrolysed to generate the volatiles, which were then contacted with two types of TiO_2 (anatase and rutile). The aim of their study was to compare the effectiveness of the two catalysts in the reduction of the substituents of monomeric phenols to simple phenols namely, cresols, phenol and xylenols. They

found that anatase was more effective than rutile in the conversion of the heavy monomeric phenols. Ma et al. [15] studied the catalytic fast pyrolysis of alkali lignin, physically mixed with several metal oxides, in amounts equivalent to 80 wt.% of the sample mass using a pyroprobe pyrolysis reactor. Without catalyst, the chemical products were a complex mixture of phenolics, while the addition of catalysts resulted in a more selective production of some chemicals, which depended on the type of catalyst applied. CuO was found to increase the selectivity of vanillin by 35%, while NiO increased the production of guaiacol by 25%, as estimated based on peak area percent comparison. Nair and Vinu [40] studied catalytic fast pyrolysis of alkaline lignin to phenols using synthesized TiO_2, ZrO_2, and CeO_2 catalysts. The lignin was physically mixed with various catalyst contents between 10-50 wt.%, and pyrolysed using Py-GC-MS. The total yields of guaiacol-derived compounds quantified by internal calibration were improved within the range of 26-37%.

Concerning the pyrolysis of lignin using alkali and alkaline earth salts, Peng et al. [37] investigated the influence of KOH, NaOH, K_2CO_3, and Na_2CO_3 mechanically blended with alkali lignin in a fixed bed pyrolysis reactor. With 10 wt.% and 20 wt.% catalyst contents, they found that the alkali carbonates produced more of methoxylated phenols, while the alkaline hydroxides catalysts produced more of non-methoxylated phenols. However, the details of the mass yields of phenols were not provided. Guo et al. [41] studied the effects of two forms of sodium incorporated into wheat straw soda-anthraquinone lignin during pyrolysis using TGA-FTIR (Fourier transform infra-red spectroscopy). The sodium was contacted with the lignin by both physical mixing (inorganic bound) and impregnation methods (organic bound) using NaOH solution (0.1 M). They found that the inorganic bound sodium enhanced the removal of the phenolic hydroxyl groups leading to increase in the yields of ether-

related products, while the organic bound sodium effectively enhanced the removal of the lignin alkyl chain, leading to increased yields of guaiacol and phenol.

From these previous studies, most of the reported works in lignin pyrolysis using metal oxides and alkali or alkaline earth salts as catalysts have used physical dry mixing with the lignin. However, impregnated catalyst could have more pronounced effect due to intimate interaction between the lignin and the catalysts [42], while requiring relatively low catalyst amount. A few studies have explored the influence of lignin isolation method on pyrolysis conversion [19,23]. Due to differences in the extent of the modification of lignin structure, isolation method was found to significantly influence phenols production. With different lignin structures, it is expected that catalytic effect will vary, thus the need to test catalysts on lignins isolated from different methods. Furthermore, phenol yields were often analysed based on peak area comparison from total ion chromatograms (TIC) obtained by GC/MS analysis. Peak areas do not provide accurate estimate of the mass yields and will at best provide information about selectivity. Instead, a quantification of the phenols yields using a calibrated method gives accurate estimates of mass yields, which is critical to determine the viability of the process [43,44].

In our previous studies [44,45], a new method was developed and found reliable to quantify condensable volatiles generated from biomass and lignin pyrolysis. The sample is converted using the thermogravimetric analyser (TGA). The generated condensable volatiles are captured in a thermal desorption (TD) tube coupled to the TGA online. The TD tube is then desorbed offline onto the gas chromatography coupled to mass spectroscopy (GC-MS), to quantify the condensable volatiles. The TGA-TD-GC-MS has several advantages, including dual roles of both volatile quantification and mechanistic monitoring of the sample mass loss during pyrolysis

[44]. Its handling of milligram-scale sample size and zero solvent requirements for treatment of condensable volatiles prior to GC-MS analysis, are also advantages for screening experiments. In this catalytic pyrolysis study, several metal oxides (Al_2O_3, Fe_2O_3, TiO_2, ZnO, CuO, MoO_3, NiO, CaO, MgO and Ni/Al_2O_3-SiO_2), and hydroxide catalysts (NaOH and KOH) were tested for the promotion of phenols production. Three sugarcane bagasse lignins isolated from different methods were impregnated with each of the respective catalysts based on 1 wt.% of the sample mass. TGA-TD-GC-MS analytical method was employed to pyrolyse the lignins and the yields of 29 compounds were quantified by internal calibration. The aim of this study is to establish the abilities of the catalysts to improve the yields and selectivities to phenol-derived chemicals.

6.2. Materials and Methods

6.2.1. Materials

6.2.1.1. Lignin Samples

Three lignin samples from sugarcane bagasse were used in this study. Soda (SD), and soda-anthraquinone (SAQ) lignins were isolated by acid precipitation and purification from black liquors obtained from these industrial processes following a method described previously [45]. Steam explosion lignin (SEH) was obtained from the steam explosion pre-treatment of sugarcane bagasse in a pilot-scale reactor conducted at 205^{o}C with a residence time of 13.5 min, followed by enzymatic hydrolysis to remove the bulk of carbohydrates, using a commercial enzyme (Viscamyl Flow) with an activity of 132 FPU/g WIS (washed insoluble solid) based on 10% (w/v) solid loading and enzyme loading of 30 FPU/g WIS. The Viscamyl Flow enzyme was supplemented with accellerase BG (185 IU β-glucosidase mL^{-1}) and multiflex

xylanase (60855 IU mL^{-1}) enzymes, equivalent to 10% of the Viscamyl Flow enzyme. All enzymes were supplied by Genencor International.

The three lignins were characterised by the following methods: proximate analysis in the TGA (Mettler Toledo TGA/DSC 1-LF1100) according to ASTM-E-1131 for moisture, ash, volatile matter and fixed carbon contents. The elemental contents (CHN) were determined by combustion method using elemental analyser TruSpec Micro (LECO). The inorganic contents (Si, Al, Ca, Fe, K, Na, S, P and Ti) were determined by X-ray fluorescence spectrometry (XRF Pan Analytical Axios PW44W/24). The residual sugars (glucose, xylose, arabinose and mannose) were determined by wet chemistry following the NREL/TP-510-42618 protocol [46]. Lastly, the molecular weight distribution was determined by gel permeation chromatography (GPC).

6.2.1.2. Catalysts

Twelve chemicals were used for catalyst screening for the pyrolysis of lignin: NaOH, Fe_2O_3, and TiO_2 purchased from ScienceWorld, KOH, CaO, ZnO, MgO and CuO purchased from Edutrade, MoO_3, Ni/Al_2O_3-SiO_2 (65 wt.% nickel supported on silica and alumina), nickel (II) nitrate ($NiNO_3.6H_2O$) purchased from Sigma Aldrich and lastly Al_2O_3 which was purchased from Fizmerk. All the catalysts were of analytical grade (purity ≥ 98%) and were used as received, except $NiNO_3.6H_2O$ which was converted to NiO by calcination in a muffle furnace at 550^oC for 5 h, according to the method described by Ma et al. 2014 [15].

6.2.1.3. Phenol standard compounds

Twenty-nine compounds purchased from Sigma-Aldrich with purity ≥ 98% were used for calibration of the GC-MS using internal calibration method. The compounds were

classified into five groups with three groups as phenols and the other two groups as anisoles and other products. The three classes of phenols were categorised according to the number of methoxy groups on the benzene unit of the monomeric phenolic compounds as syringol type (S-type with two methoxy groups), guaiacol type (G-type with one methoxy group), and phenol type (P-type without methoxy group). Therefore, the compounds under the five classes are grouped as follows: S-type (syringol, 4-methylsyringol, allylsyringol, and acetosyringone), G-type (guaiacol, creosol, 4-ethylguaiacol, 4-vinylguaiacol, eugenol, 4-propylguaiacol, trans-isoeugenol, isoeugenol, vanillin, acetoguaiacone, 3-methoxycatechol and 3-hydroxy-4-methoxyacetophenone), P-type (phenol, o-cresol, 2,6-dimethylphenol, p+m cresol, 2,4-xylenol, catechol and 4-ethylphenol), anisole-type (anisole, 4-methylanisole, and ethenylanisole), and Other products (toluene and furfural). The chemical structures of the various compounds are presented as supplementary material Figure S 6-1.

6.2.2. Methods

6.2.2.1. Lignin Impregnation with Catalysts

Each lignin sample considered in this study was impregnated with 1 wt.% catalyst content based on lignin mass. The impregnation was performed by the addition of 20 mL of distilled water mixed with the catalyst to each lignin sample (1 g) in a 150 mL Schott bottle, and then stirred on a Velp Scientifica multiple stirring system set at 300 rpm at room temperature for 24 h. The homogeneous solutions of the samples formed were then placed on magnetic stirrer hotplates set at 80^{o}C and 100 rpm to evaporate the water until slurries resulting in resistive movements of the stirring magnets in the bottles were reached. The stirring magnets were removed with spatula, and the slurries were dried in the oven at 100^{o}C for 24 h. The dried samples were ground

using pestle and mortar until particle sizes of ≤ 425 µm were obtained, and then packaged in sealed bags prior to pyrolysis experiments.

6.2.2.2. Catalytic pyrolysis experiments using TGA-TD-GC-MS

Catalytic pyrolysis experiments were conducted according to recently developed method described in a previous work [45]. In brief, thermogravimetric analysis (TGA) using a Mettler Toledo TGA/DSC 1-LF1100 system was used to pyrolyse approximately 10 mg of lignin samples, with a temperature programme from 30 ^{o}C to 600 ^{o}C at a heating rate of 10 ^{o}C min^{-1} in a stream of argon (baseline 5.0 Afrox) used as carrier gas flowing at 70 mLmin^{-1}. The volatiles generated during the pyrolysis regime were captured online in a stainless thermal desorption (TD) tube (C1-AAXX-5003-MARKES International, UK). After an injection of a 3 µl of internal standard solution (6.1 g/L 2-octanol diluted in ACS grade acetone with purity >99.9% from Sigma-Aldrich), the TD tube was desorbed into a GC/MS via a thermal desorption (Unity 2) system. The TD tube was heated to 320 ^{o}C for 10 min via the thermal desorption (Unity 2) system. Removal of the volatiles from the TD tube was achieved using a grade 5.0 (Afrox SA) helium gas flowing at 10 mL min^{-1} and a split flow of 30 mL min^{-1}. The volatiles were transferred from the trap section of the Unity system at 320 ^{o}C from the trap section of the Unity system for 10 min aided by a helium gas flowing at the rate of 1.5 mL min^{-1} into the GC-MS transfer line under a split flow of 30 mL min^{-1}. Analysis of the volatiles were performed on an Agilent Technology 7890A GC coupled to an Agilent Technologies 5975C MS. The GC was equipped with a 60 m x 0.25 mm ID x 0.25 µm FT capillary column (14% cyanopropylphenyl-methylpolysiloxane), model ZB-1701 (Agilent Technology). The GC oven temperature programme began at 45 ^{o}C for 10 min and then increased at a heating rate of 7^{o}C/min to 260 ^{o}C. The MS was operated in EI mode with an ion-source energy of

70 eV. The detected mass-to-charge (m/z) ratio ranged from 20 to 500. Phenols calibration was done by preparing mixtures of standard compounds of known concentrations (29 compounds). Dilutions were done using ACS grade acetone with purity >99.9%. Thereafter, following the injection of 3 µL of the standard solution and 3 µL of internal standard (6.1 g/L 2-octanol in acetone) in a TD tube, the same TD-GC-MS method was used, and the calibration curves were prepared. All the phenolic compounds were identified according to NIST 2011 MS library and by comparison of the retention time with those of the standard compounds. For reproducibility and accuracy of the data, all the experiments were performed at least in duplicate for each lignin/catalyst couple. The average relative standard deviation (RSD) on the total yields of the phenols was 13%. A t-test (two samples assuming equal variance), was used as a statistical analysis method to check if the phenols yields obtained with the various catalysts were statistically different from the yields obtained without catalyst.

6.3. Results and Discussion

6.3.1. Compositional characteristics of lignin

The compositional characteristics of the studied lignins are detailed in Table 6-1. The proximate and ultimate analyses results showed that both soda lignins (SD and SAQ) had similar volatile matter (67%), fixed carbon (30-31%), carbon (C) (61%), hydrogen (H) (5.5 wt.%), nitrogen (N) (0.2-0.3 wt.%), and sulphur (S) (3.0 wt.%) contents. Most of the organic elements were found in slightly lower content in SEH due to its higher ash content (7.7 wt.% versus 4.5 wt.% and 2.0 wt.% for SD and SAQ respectively). The content of nitrogen in SEH lignin (2.0 wt.%) was more than those of SD and SAQ lignins (0.2 wt.% and 0.3 wt.%) respectively, which was attributed to the presence of residual

enzymes used during the hydrolysis step to remove the carbohydrate fraction from the washed insoluble solid (WIS) material to produce SEH lignin. For the three lignins, silicate (SiO_2) was found to be the main inorganic component (3.9 wt.%, 1.1 wt.% and 5.5 wt.%) for SD, SAQ, and SEH lignins respectively), which is characteristic of non-woody biomasses, consistent with literature [45]. For the residual sugars (Table 6-1), SAQ lignin had higher amount (10.1 wt.%) than SD and SEH lignins (both 6.4 wt.%), of which the difference could be attributed to the extent of lignin carbohydrate complexes (LCC) removal during the process of isolation [47].

In terms of molecular weight distributions, SD and SAQ had molecular weights (M_w) of 7779 Da and 3253 Da respectively, with polydispersity index (PDI) of 3.1 and 1.9 respectively (Table 6-1), which shows that SD lignin had less uniform molecular chain length than SAQ lignins [48]. For SEH lignin, the acetylated form could not completely dissolve in THF during sample preparation prior to the GPC analysis and therefore, its molecular weight and PDI could not be determined.

Table 6-1: Proximate analysis, ultimate analysis, total sugars, inorganic content, and molecular weights for SD, SAQ and SEH lignins (wt.% dry basis)

Lignin name	Volatile Matter	Fixed Carbon	Ash	C	H	N	S	Total sugars		
SD	66.7	29.6	4.5	61.2	5.5	0.2	2.9	6.4		
SAQ	66.7	30.7	2.0	61.2	5.5	0.3	3.0	10.1		
SEH	62.8	29.8	8.0	58.2	5.1	2.0	bdl	6.4		
	Inorganic content							**Molecular weight**		
	SiO_2	**Al**	**Ca**	**Fe**	**K**	**Na**	**P**	**Mw (g/mol)**	**Mn (g/mol)**	**Mw/Mn (PD)**
SD	3.9	0.6	bdl	0.1	bdl	< 0.1	< 0.1	7779	2513	3.1
SAQ	1.1	0.2	0.0	< 0.1	bdl	0.1	bdl	3253	1721	1.9
SEH	5.5	0.4	0.1	0.3	0.1	0.1	bdl	-	-	-

6.3.2. Influence of catalysts on the thermal behaviour of the lignin samples

In this study, the pyrolysis of the lignins impregnated with catalysts were carried out at 600 ^{o}C using the TGA based on a heating rate of 10 ^{o}C min^{-1}. The differential thermogravimetric (dTG) curves corresponding to the rate of mass loss for both the non-catalytic and catalytic conversion are shown in Figure 6-1a-f. The respective TG curves showing the evolution of the sample mass are given as supplementary material Figure S 6-2a-d. A summary of the peak temperatures and char yields produced during the non-catalytic and catalytic pyrolysis of the three lignins are detailed in Table 6-2. The dTG curves show that the decomposition of the lignins occurred in a wide temperature range from 150 ^{o}C to 600 ^{o}C. In Figure 6-1a, for non-catalytic pyrolysis, it is observed that the dTG curves for SD and SAQ lignins are composed of a first peak starting to be significant around 200 °C and a second peak with a maximum around 380 °C, while the curve corresponding to SEH lignin only showed a broad main peak with a maximum at 366 ^{o}C. This means that SEH lignin contained a lower amount of chemical groups unstable around 200 °C. The difference is probably related to the pretreatment conditions, more severe for SEH lignin due to the combination of steam and temperature of 205 ^{o}C, when compared to the range of temperature (150-200 ^{o}C) mostly applied by the pulping industries for lignin removal [49]. This resulted in reduced number of thermally unstable groups in SEH lignin and hence less volatiles were produced within this temperature range. The maximum temperature of weight loss between 366 and 385 ^{o}C depending on lignin type, was within the range usually reported for the main decomposition of lignin structure [34]. It corresponds to the main release of the phenolic products, due to higher rate of bond cleavage between the monomer units [50]. The non-catalytic pyrolysis of SEH lignins resulted in 37.4 wt.% char yield (expressed on dry and ash-free basis). For the other

two lignins, the DTG curves were composed of two main peaks of weight loss occurring at 272 ºC and 376 ºC for SD, and 253 ºC and 385 ºC for SAQ. The mass loss corresponding to the first decomposition stage was approximately 13 % and 12% respectively. Conversion of the residual sugar probably contributed to this peak, as with lignocellulosic sample mass loss at temperature lower than 300 °C is mostly attributed to hemicelluloses degradation [22,51]. However, given that the amount of mass lost exceeded the amount of residual sugar present in the lignin samples (6.4 wt.% and 10.1 wt.% respectively), the mass loss was also partly attributed to lignin decomposition. The char yields generated from the non-catalytic pyrolysis of SD and SAQ lignins were about 35.9% and 36.5%, which are slightly lower than that of SEH lignin. These results (on dry ash free basis) are consistent with the ratios of fixed carbon (FC) to volatile matter (VM) (Table 6-1), the higher the ratio, the higher the char yield.

With regards to the dTG curves of catalytic pyrolysis with the different catalysts, for SEH lignin (Figure 6-1b), all the dTG curves were still composed of a single weight loss peak with maximum between 337 ºC and 368 ºC. The peak maximum of dTG curves for NaOH and KOH occurred at lower temperatures (both approximately at 337ºC) than for the metal oxides (362-368ºC). This suggests that the catalytic effect of the two hydroxides made the conversion of SEH lignin to occur at lower temperatures than for the metal oxide catalysts. The temperature reductive effects of impregnated sodium and potassium salts during pyrolysis have been reported in several literatures [41,52,53]. This phenomenon was associated with the effective catalytic role during pyrolysis or to biomass swelling during biomass impregnation [53]. As the phenomenon was not observed with the metal oxides (also mixed via impregnation), the temperature change can be attributed to the hydroxides catalytic

effect. With higher reactivity in terms of conversion temperature, more depolymerisation and a higher extent of degradation in terms of mass loss could have been expected. However, with respect to the char yields obtained with the various catalysts from SEH lignin, higher amounts were obtained with NaOH (40.1 wt.%) and KOH (40.6 wt.%), while those with the metal oxides (37.3-39.6 wt.%) were relatively closer to that of the non-catalytic char (37.4 wt.%). This suggested that some recombination reactions leading to the formation of secondary char were catalysed, especially with the metal hydroxides oxides. From previous studies, the inclusion of catalysts such as NiO, TiO_2, KCl, NaCl, Na_2CO_3, K_2CO_3, NaOH, KOH, etc. during biomass pyrolysis were also found to promote recombination reactions, leading to the formation of more char than without catalyst [40,52]. Due to the existence of recombination reaction, it appeared that the char yield alone cannot be used to assess the effect of the catalyst on lignin depolymerisation and phenols production.

For SD lignin (Figure 6-1c-d), all the samples were characterised by two distinct weight loss peaks, except for the samples impregnated with CaO and NaOH, which presence exhibited one broad peak within the ranges of 341-372 ^oC and 331-350 ^oC respectively (Figure 6-1c). The intensities of the first weight loss peaks for Ni-Al_2O_3-SiO_2, MgO, ZnO, and KOH occurring at 288 ^oC, 313 ^oC, 282 ^oC and 307 ^oC respectively, which corresponded to 14%, 17%, 14% and 19% mass losses respectively, were stronger than for the remaining catalysts (9-12% mass losses). This suggests that their catalytic effects caused higher volatile release within this temperature range than other catalysts, with KOH producing the most pronounced effect. About 36.2-40.7 wt.% (dry, ash, and catalyst-free basis) of char yields were generated during catalytic pyrolysis of SD lignin, as presented in Table 6-2. These are much higher than the char yield obtained without catalysts (35.9 wt.%) except that of

KOH catalysed pyrolysis that was more similar to the one without catalyst (36.2 wt.%). Again, the formation of secondary char at the surface of the catalyst can explain this trend. The lower char yield for KOH than for other catalysts suggests that it had a promoting effect on the depolymerisation of SD lignin.

In the case of SAQ lignin (Figure 6-1e-f), the dTG curves are composed of two major peaks of weight loss for all the catalysts. With the different catalysts, the intensities of the first weight loss peaks were found to be higher than without catalysts. With CaO, MgO, NaOH and KOH, the peaks which appeared at 313 ^{o}C, 306 ^{o}C, and 300 ^{o}C (both NaOH and KOH) respectively, were remarkably higher than for other catalysts. These corresponded to mass losses of 23%, 22%, 19% and 21% respectively, as compared to the 9-15% for the remaining catalysts. Furthermore, the intensities of the peaks corresponding to the first decomposition stage became even higher than those ones in the second decomposition stage (4.3 vs 3.3 %/min), (4.0 vs 3.2 %/min), (3.6 vs 3.2 %/min), and (3.8 vs 3.3 %/min) respectively, evidencing a more pronounced lignin conversion in the first decomposition stage than in the second decomposition stage by these catalysts. In terms of the char yields, those ones generated with CaO, MgO, Fe_2O_3, NaOH, and KOH were the lowest (Table 6-2), with that of CaO (34.9 wt.%) even lower than the one generated without catalyst (36.6 wt.%). This signals that SAQ depolymerisation was particularly enhanced by CaO [52,54]. Based on these results, the presence of the catalysts resulted in significant modification in conversion mechanisms, thus, changes in phenols distribution were expected.

Table 6-2: Mass loss peak temperatures and char yields obtained during the pyrolysis of SD, SAQ, and SEH lignins with and without catalysts

	First dTG peaks (°C)												
	No Catalyst	Al_2O_3	Ni-Al_2O_3-SiO_2	NiO	CaO	CuO	MgO	Fe_2O_3	MoO_3	ZnO	NaOH	KOH	TiO_2
SD	271.9	255.3	288.3	273.5	-	267.4	312.9	262.3	251.3	281.5	331.4	307.1	262.0
SAQ	252.6	266.7	273.3	249.0	312.7	241.4	305.7	252.6	226.3	272.5	300.0	300.0	234.5
SEH	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
	Second dTG peaks (°C)												
	No Catalyst	Al_2O_3	Ni-Al_2O_3-SiO_2	NiO	CaO	CuO	MgO	Fe_2O_3	MoO_3	ZnO	NaOH	KOH	TiO_2
SD	376.1	376.5	373.1	376.4	346-372	376.2	371.7	374.1	377.9	371.8	348.9	371.7	377.7
SAQ	384.9	384.1	383.4	383.7	381.5	383.6	383.5	381.5	383.4	378.9	372.1	381.2	383.7
SEH	365.7	367.7	367.9	367.2	367.3	367.4	362.3	366.3	366.7	367.9	336.5	336.5	367.3
	Char Yield (wt.% dry, ash, catalysts-free basis)												
	No Catalyst	Al_2O_3	Ni-Al_2O_3-SiO_2	NiO	CaO	CuO	MgO	Fe_2O_3	MoO_3	ZnO	NaOH	KOH	TiO_2
SD	35.9	39.9	38.5	38.3	37.8	39.7	39.9	38.4	40.7	39.4	39.4	36.2	39.5
SAQ	36.5	40.1	38.6	38.4	34.9	39.3	36.5	36.4	41.9	39.4	36.7	35.6	39.8
SEH	37.4	38.4	37.9	37.6	37.3	38.2	37.3	37.7	39.6	38.2	40.6	40.1	38.5

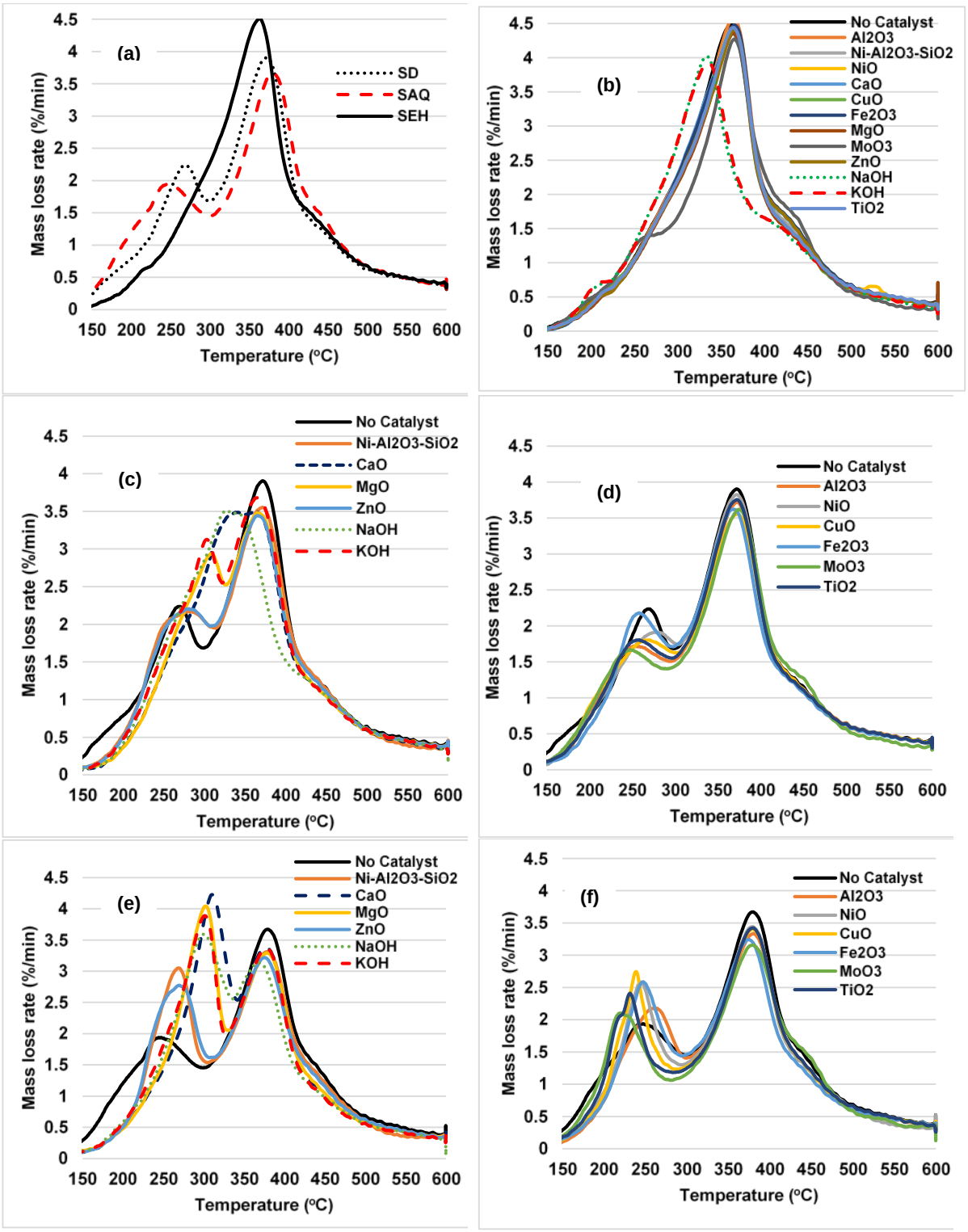

Figure 6-7a-f: DTG curves of the conversion of SEH, SD and SAQ lignins without catalyst (a), and with catalysts (b) for SEH, (c-d) for SD lignin, and (e-f) for SAQ lignin, pyrolysed at a heating rate of 10 °C/min

6.3.3. Phenols from catalytic pyrolysis

6.3.3.1. Effects of the various catalysts on the total yields of phenols

GC-MS analysis of the volatiles produced from the TGA pyrolysis was performed to determine the yields of the phenolic products from SD, SAQ, and SEH lignins. The details of the yields of 29 compounds quantified by internal calibration are listed in Tables 6-3, 6-4 and 6-5 for SD, SAQ, and SEH lignins respectively. Some of the phenolic compounds were excluded from Tables 6-3, 6-4 and 6-5, due to low yields (≤ 0.03 wt.%). They include trans-isoeugenol, eugenol, propylguaiacol, acetoguaiacone, 3-hydroxy-4-methoxyacetophenone, 2,6-dimethylphenol, ethenylanisole, and catechol. Non-catalytic pyrolysis of SD, SAQ, and SEH lignins produced total phenols yield of 8.9 wt.%, 5.2 wt.%, and 6.0 wt.% respectively. In this study, the total yields of phenols obtained from the three lignins were within the range reported in literature (4.3-18.0 wt.%) [2,21,40,55,56].

The differences in the total yields of phenols among the three lignin types (Tables 6-3, 6-4 and 6-5) could be attributed to the extent of degradation incurred during lignocellulose processing and subsequent lignin isolation. For example, during soda pulping, some of the lignin phenolic α- and β-O-4 bonds are cleaved [57]. The addition of anthraquinone as catalyst to the soda pulping process, named as soda-anthraquinone (SAQ) pulping is known to enhanced the breakage of interunit bonds [57,58], consistent with the fact that SAQ lignin contained lower molecular weight molecules than SD lignin as observed from GPC results (Table 6-1). Therefore, a likely reason for the low yield of total phenols from SAQ lignin (5.2 wt.%) as compared to that of the SD (8.9 wt.%) could be attributed to more stable structure of SAQ lignin, as most of the interunit bonds (known to be thermally unstable and react

between 200 and 400 °C) were cleaved during pulping, leaving behind some bonds more resistant to pyrolysis during conversion [19].

The total phenols yield change obtained with the various catalysts are shown in Tables 6-3, 6-4, and 6-5 for SD, SAQ, and SEH lignins respectively. Additionally, the yield increases (%) obtained with the various catalysts are presented in Figure 6-2. From Figure 6-2, it can be observed that most of the screened catalysts increased the total yields of phenols, except for CuO, CaO, MgO, MoO_3, NaOH and TiO_2 for SD lignin only, and ZnO for both SAQ and SEH lignins. However, not all the yield increases were found to be statistically significant. For SD lignin, only the total yield of phenols produced with KOH (11.2 wt.%), as compared to the non-catalytic yield (8.9 wt.%), equivalent to 26% increase was considered as indicative of significant improvement. For SAQ lignin, all the catalysts, except Al_2O_3, NiO, MoO_3, ZnO, and TiO_2 produced statistically significant increases of phenols yields. The highest yield of total phenols was produced with CaO (8.2 wt.%), equivalent to 60% increase, as compared to the non-catalytic pyrolysis yield (p-value of 0.01). Similarly, for SEH lignin, all the catalysts except Al_2O_3, NiO, ZnO, and TiO_2 produced statistically significant yield increases of total phenols. Fe_2O_3 had the most significant effect by increasing the total yield of phenols from 6.0 ± 0.1 wt.% to 8.6 ± 0.1 wt.%, equivalent to 43 % increase (p-value of 0.02). The performance of KOH for SD lignin and CaO for SAQ lignin are well correlated with their respective peak intensities in the first decomposition stages, which were the highest (Figure 6-1c and e), indicative of catalytic effect on some primary reactions occurring during this stage. From the few reported studies in literature, these results are quite lower than for Nair and Vinu [40], who obtained a total phenols yield increase of about 106% at 10 wt.% catalyst content. However, the significant phenols yield increases obtained in this screening

study with low catalyst content (1 wt.%) demonstrates the effectiveness of the impregnation method, due to the intimate contact of the catalysts with the lignins. Regarding the catalytic effect of Fe_2O_3 with SEH lignin, no particular effect could be predicted based on the dTG curve. It can be deduced that the main effect of Fe_2O_3 was probably the cracking of volatiles (secondary reaction), which converted some oligomers into phenols.

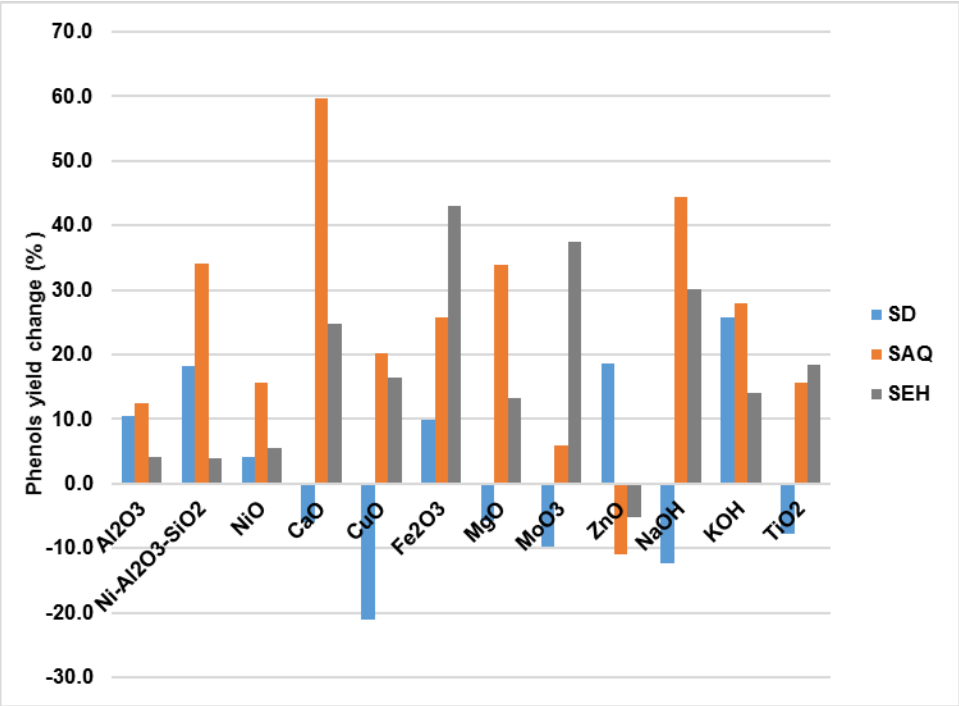

Figure 6-2: Phenols yields change (% based on dry, ash, catalyst-free sample) obtained from catalytic pyrolysis of SD, SAQ, and SEH lignins.

6.3.3.2. Effects of the various catalysts on the yields of the phenolic compounds

The changes effected by the catalysts during lignins pyrolysis were also considered in terms of the distributions of the monomeric phenol products, which were grouped into syringol type (S-type), guaiacol type (G-type), and phenol type (P-type) compounds based on the number of methoxy substituents on the aromatic ring as detailed in Tables 6-3, 6-4, and 6-5 for SD, SAQ, and SEH lignins respectively. The total yields

of the three groups of compounds are illustrated in Figure 6-3a-c. It can be observed that for the pyrolysis of the three lignins without catalysts, the G-type phenols were more predominant (around 50%) than the S-type and P-type phenols. The similar relative amounts were expected as the three lignins originated from the same biomass type (sugarcane bagasse) [45].

For the catalytic pyrolysis of the three lignins, the catalysts displayed different effects on the yields of the S-type, G-type and P-type phenols as compared to the non-catalytic yield (Figure 6-3a-c). For SD lignin (Figure 6-3a) and based on the statistical analysis using t-test, all the catalysts had minimal influence on the production of S-type and G-type phenols except KOH. The yields of the S-type and G-type phenols were increased by KOH from 1.3 wt.% and 4.4 wt.% to 1.8 wt.% and 5.7 wt.% respectively. These yield increases were equivalent to 34% and 32% respectively, while the value was only 14% for H-type phenols. The main S-type and G-type compounds obtained in significant amounts from SD lignin were syringol, guaiacol and 4-vinylguaiacol (Table 6-3), which are chemicals used in cosmetic, fragrance, pharmaceutical and food industries and have market values around 5000 US$/ton [59]. Their yields were significantly increased by KOH from 0.7 wt.%, 1.1 wt.%, and 2.0 wt.% to 1.0 wt.%, 1.4 wt.% and 2.8 wt.%, equivalent to 41%, 32%, and 43% increases respectively. The production of S-type and G-type phenolic compounds by KOH suggests that the catalyst promoted lignin depolymerisation at a lower temperature prior to extensive conversion of the methoxy groups [60]. This is evident by the intensity of the dTG peak in the first decomposition stage, which was higher than for other catalysts (Figure 6-1c). Hence, KOH was the most selective towards the production of S-type and G-type phenols from SD lignin.

For SAQ lignin, all the catalysts significantly increased the yields of S-type and G-type phenols except MoO_3 and ZnO (both S-type and G-type phenols), and Al_2O_3, NiO and TiO_2 (which were not significant only for G-type phenols). The catalysts with the most significant effects on the yields increases of S-type and G-type phenols were Ni-Al_2O_3-SiO_2, NaOH, KOH, CaO, and MgO (Figure 6-3b). Similar to the trend observed with KOH with the SD lignin, the effects of these catalysts resulted in the release of more volatiles in the first decomposition stage from SAQ lignin than other catalysts, as evident by the intensities of their respective DTG peaks (Figure 6-1e). Therefore, they promoted low temperature depolymerisations leading to an increased production of S-type and G-type phenols. The trend was more pronounced for CaO, which increased the yields of S-type and G-type phenols significantly, from 0.6 wt.% and 2.6 wt.% to 1.1 wt.% and 4.2 wt.%, equivalent to 76% and 64% respectively. Like the SD lignin, syringol, guaiacol, and 4-vinylguaiacol were the S-type and G-type phenols obtained in higher amounts. NaOH produced the highest yields of syringol and guaiacol by increasing the yields from 0.28 wt.% and 0.57 wt.% to 0.62 wt.% (p-value = 0.03) and 1.10 wt.% (p-value = 0.01), equivalent to 121% and 93% respectively. CaO produced the highest yield of 4-vinylguaicol by increasing the yield from 0.74 wt.% to 1.36 wt.%, equivalent to 84%.

For SEH lignin, these same catalysts produced the most effects on S-type and G-type compounds except Al_2O_3, NiO, MgO, ZnO (not significant for both S-type and G-type), and TiO_2 (not significant for G-type). The highest effects were obtained with Fe_2O_3 and MoO_3, both leading to yield increases of S-type and G-type phenols in the range of 42-45%. Unlike the SD and SAQ lignins, the correlation with the dTG curves was not obvious, given that no particular modification of the curves was observed with these catalysts (Figure 6-1b). Like both SD and SAQ lignins, syringol, guaiacol,

and 4-vinylguaicol were the main S-type and G-type phenols produced from SEH lignin. As observed with SAQ lignin, NaOH produced the highest effect on the production of syringol and guaiacol of which their yields were significantly increased from 0.4 wt.% and 0.8 wt.% to 0.7 wt.% and 1.4 wt.% respectively, equivalent to 75% increases (for both compounds). Fe_2O_3 and MoO_3 produced the most effects on 4-vinylguaicol as they both increased the yield from 1.3 wt.% to 2.0 wt.%, equivalent to approximately 54%. Nair and Vinu [40] (at 10 wt.% catalyst content) reported increases in the yields of guaiacol and vinylguaiacol within the range of 64-106% and 41-62% respectively. Hence, the yields increase of guaiacol and vinylguaiacol obtained in this study from SD lignin (32% and 43%), SAQ lignin (93% and 83%), and SEH lignin (75% and 54%) respectively, were comparable with previous study. This demonstrates that when impregnated, catalysts are quite effective to improve the yields of some specific compounds.

Regarding the P-type phenols the highest yield without catalyst was obtained with SD lignin. With the addition of the various catalysts, only Al_2O_3 and ZnO increased the yield of P-type phenols significantly from 3.2 wt.% to 4.2 wt.% and 4.4 wt.%, equivalent to 29% and 36% respectively. P-type phenols can be produced via depolymerisation of p-hydroxyphenyl (H) units or through the cracking of the methoxy groups attached to the aromatic ring of phenols derived from guaiacyl (G) and syringyl (S) units (Table 6-3). With the SAQ lignin (Figure 6-3b), the yield increases obtained with Ni-Al_2O_3-SiO_2, CaO, CuO, Fe_2O_3, MgO, and NaOH were statistically significant (Figure 6-3b). The highest effect was produced with CaO with yield increase from 2.0 wt.% to 2.9 wt.%, equivalent to 49% (p-value of 0.01). Since CaO was also observed to be the most selective towards the production of S-type and G-type phenols from SAQ lignin, it thus shows that CaO produced the most influence

on the depolymerisation of SAQ lignin. The enhancement of depolymerisation reactions by CaO agrees with its char yield (35 wt.%), which was lower than without catalyst (37 wt.%). For SEH lignin, the yield increases obtained with CaO, Fe_2O_3, MoO_3, NaOH, and KOH were found to be statistically significant (Figure 6-3c). The selectivity of NaOH towards the production of the P-type phenols was also observed by Peng et al. [37]. The highest effect was produced with Fe_2O_3 with yield increase from 2.13 wt.% to 2.96 wt.%, equivalent to 39% increase. Among the P-type compounds, phenol was the most abundant, of which ZnO, CaO, and NaOH produced the most statistically significant yields increases equivalent to 40%, 53% and 59% from SD, SAQ, and SEH lignins respectively, (Tables 6-3-5). The highest yield of phenol was 1.8 wt.% obtained with SD lignin and ZnO catalyst.

In another approach to investigate the influences of the catalysts on the conversion of lignin, the quantified pyrolytic phenolic products were classified into four groups as C_0, C_1, C_2, and C_3 based on the number of carbons remaining on the alkyl chain in para position of the hydroxyl group as shown in supplementary Tables S6-1, S6-2, and S6-3, and their various proportions are presented in Figure 6-4a-c. C_0 phenols are produced via the cleavage between the aromatic ring and the alkyl chain. Based on this grouping, the C_0 phenols account for the largest proportions of the phenols classes of which the most dominant compounds were syringol, guaiacol, phenol and o-cresol. Considering the effects of the various catalysts (Figure 6-4a-c), a clear change was observed for the C_0 phenols for SEH lignin catalysed by the two hydroxides (Figure 6-4c). The proportions of the C_o phenols were remarkably increased from 42.8% to 54.9% and 55.9% by NaOH and KOH respectively. Although the correlation is unsure, these two hydroxides catalyst were observed to display catalytic roles that caused the conversion of SEH lignin to occur at lower temperatures than with the

metal oxides (Figure 6-1b). For SD lignin, Al_2O_3 and NaOH produced the highest effects as they increased the proportions of C_0 phenols from 42% to 46% (for both). With SAQ lignin, KOH produced the most effect by increasing the proportion from 46.1% to 49.2%. From these results, NaOH has demonstrated to be particularly selective towards the production of C_0 phenols. For C_1 phenols, which formation involves the cleavage between the carbon atoms on the α and β positions, the two hydroxides decreased the proportions with the three lignin samples, while majority of the metal oxides had minimal impacts except MoO_3 which significantly increased the proportion from 23.7% to 27.5% for SEH lignin. The main C_1 phenols were creosol, methylsyringol, and p-cresol. Regarding the C_2 and C_3 phenols, no clear trend could be observed. Overall, the most notable change was the C_0 phenols of SEH lignin of which the two hydroxide catalysts produced the highest proportions.

While this study at analytical scale evidenced the benefit of using catalyst, more investigation will be required when scaling-up the conversion. Of particular importance are the influence of particle heating rate and the risk of phenols recombination into oligomers. Considering the former, increasing heating rate is known to lead to higher bio-oil yield (provided final temperature is not too high) [61]. However, relatively high bio-oil yield can be due to substantial production of oligomers [61]. The heating rate should be optimised in order to limit the formation of oligomers and/or promote their cracking into monomeric phenols by the catalyst. Phenols recombination has been observed in volatile phase (in the hot part of the reactor) and in liquid phase (following condensation) . In most of the lignin pyrolysis studies, using Py-GC/MS with sample mass lower than 1 mg as in our study, the volatiles products were highly diluted, which probably limited the contact between the phenols. In addition, the volatiles were analysed by GC/MS without being condensed

as liquid. Scaling-up is required in order to assess the impact of recombination reactions on phenols yields.

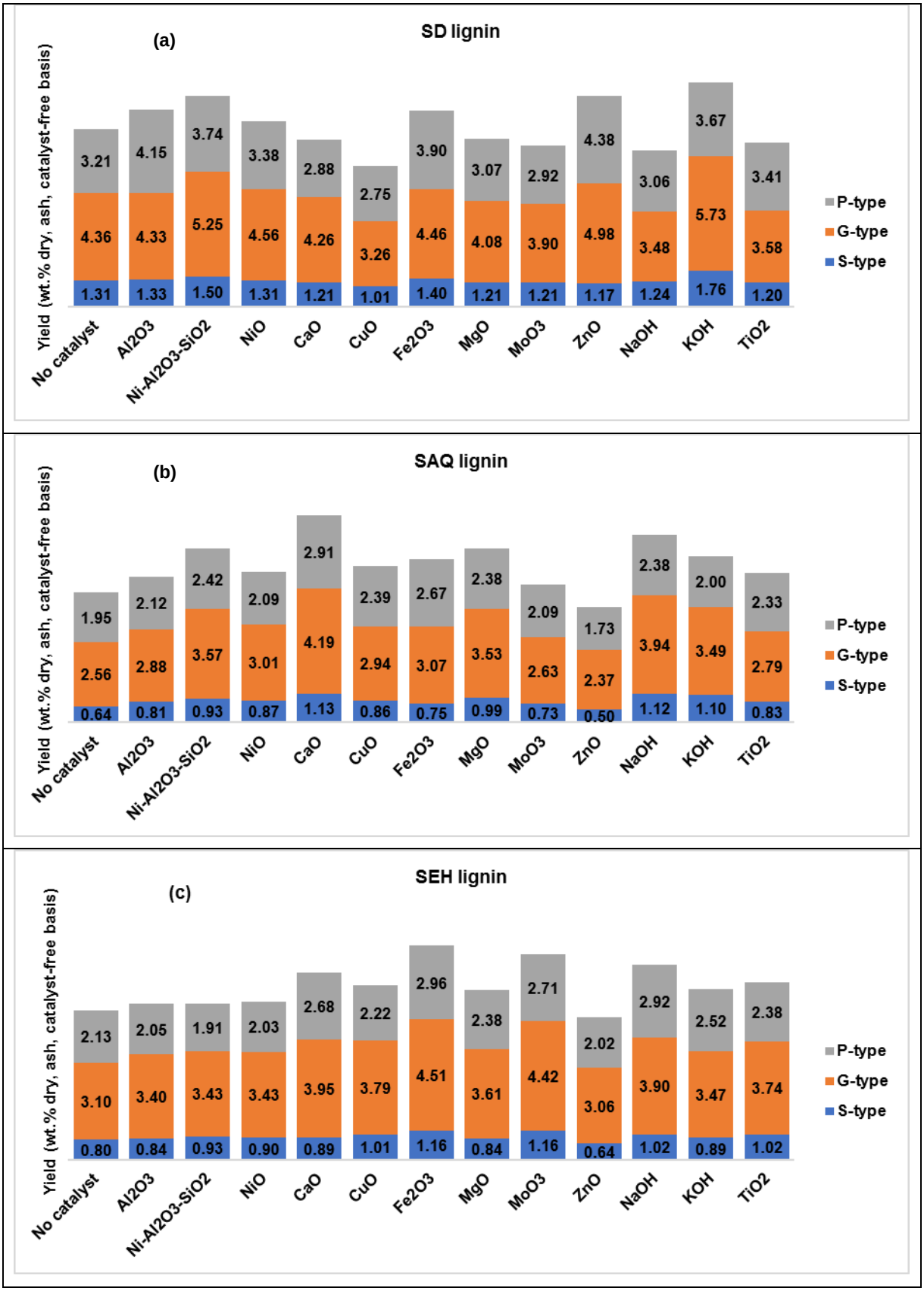

Figure 6-3a-c: Yields of S-type, G-type, and P-type from catalytic pyrolysis of SD lignin (a), SAQ lignin (b), and SEH lignin (c).

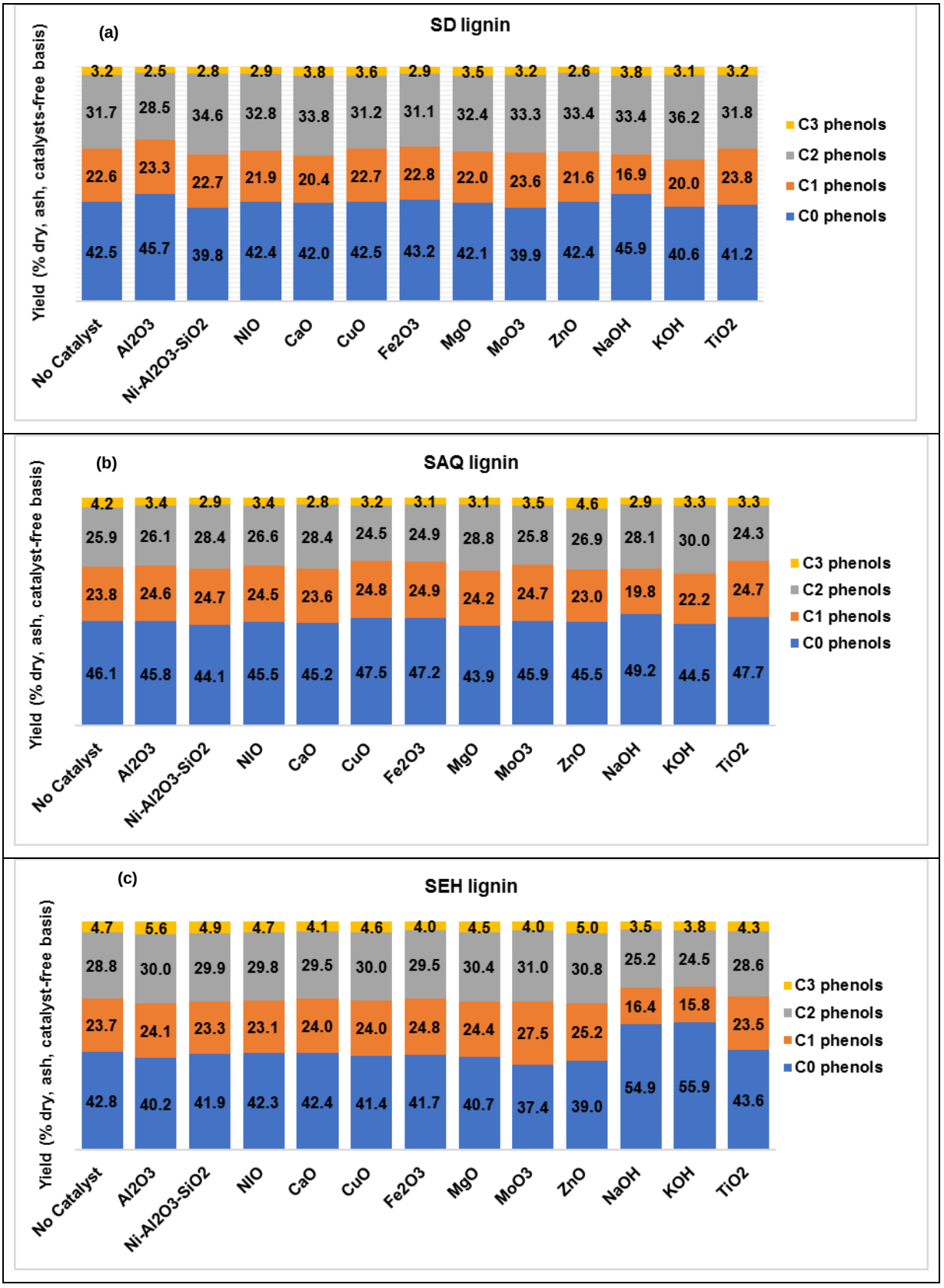

Figure 6-4a-c: Distribution of the phenols obtained from catalytic pyrolysis of SD, SAQ, SEH lignins based on the number of atoms of carbon on the alkyl chain in para position of the hydroxyl group.

Table 6-3: Yields of monomeric products (wt.% dry, ash, catalyst-free basis) from catalytic pyrolysis of SD lignin

Compound	No catalyst	Al_2O_3	Ni-Al_2O_3-SiO_2	NiO	CaO	CuO	Fe_2O_3	MgO	MoO_3	ZnO	NaOH	KOH	TiO_2
Syringol-type													
Syringol	0.68	0.70	0.72	0.69	0.63	0.52	0.71	0.60	0.58	0.64	0.87	0.96	0.62
4-methylsyringol	0.47	0.47	0.53	0.46	0.42	0.35	0.49	0.45	0.46	0.43	0.24	0.58	0.43
Acetosyringone	0.16	0.16	0.18	0.16	0.17	0.13	0.20	0.17	0.16	0.11	0.13	0.22	0.15
Sum	**1.31**	**1.33**	**1.50**	**1.31**	**1.21**	**1.01**	**1.40**	**1.21**	**1.21**	**1.17**	**1.24**	**1.76**	**1.20**
Guaiacol-type													
Anisole	0.14	0.21	0.23	0.17	0.16	0.15	0.23	0.19	0.18	0.03	0.16	0.10	0.16
4-methylanisole	0.12	0.16	0.15	0.14	0.12	0.10	0.14	0.12	0.10	0.18	0.13	0.13	0.12
Guaiacol	1.06	1.29	1.27	1.19	1.07	0.76	1.15	1.04	0.96	1.24	0.55	1.40	0.75
creosol	0.50	0.59	0.66	0.56	0.45	0.43	0.55	0.49	0.53	0.58	0.29	0.59	0.50
4-ethylguaiacol	0.23	0.38	0.36	0.27	0.26	0.23	0.33	0.31	0.25	0.35	0.25	0.32	0.29
4-vinylguaiacol	2.01	1.40	2.25	1.94	1.85	1.29	1.74	1.59	1.59	2.29	1.79	2.80	1.47
Isoeugenol	0.22	0.21	0.24	0.22	0.25	0.21	0.23	0.24	0.21	0.23	0.24	0.28	0.21
Acetoguaiacone	0.08	0.09	0.10	0.08	0.09	0.08	0.10	0.10	0.09	0.08	0.07	0.11	0.08
Sum	**4.36**	**4.33**	**5.25**	**4.56**	**4.26**	**3.26**	**4.46**	**4.08**	**3.90**	**4.98**	**3.48**	**5.73**	**3.58**
Phenol-type													
Phenol	1.28	1.66	1.52	1.39	1.23	1.18	1.58	1.27	1.17	1.79	1.44	1.54	1.35
o-cresol	0.75	0.94	0.77	0.76	0.70	0.60	0.88	0.72	0.57	0.99	0.75	0.83	0.76
p+m-cresol	0.73	0.90	0.87	0.75	0.57	0.59	0.87	0.64	0.72	0.94	0.50	0.78	0.77
2,4-xylenol	0.11	0.13	0.12	0.11	0.09	0.08	0.13	0.09	0.09	0.15	0.09	0.12	0.12
4-ethylphenol	0.34	0.52	0.48	0.37	0.29	0.30	0.44	0.35	0.37	0.52	0.28	0.40	0.42
Sum	**3.21**	**4.15**	**3.74**	**3.38**	**2.88**	**2.75**	**3.90**	**3.07**	**2.92**	**4.38**	**3.06**	**3.67**	**3.41**
Others													
Toluene	0.29	0.33	0.33	0.29	0.27	0.24	0.34	0.29	0.40	0.35	0.30	0.32	0.28
Furfural	1.88	4.55	2.93	2.44	0.86	2.03	3.12	1.72	2.37	2.44	0.43	1.57	2.88
Total Phenols	**8.88**	**9.81**	**10.49**	**9.25**	**8.35**	**7.01**	**9.77**	**8.36**	**8.02**	**10.53**	**7.79**	**11.17**	**8.19**

Table 6-4: Yields of monomeric products (wt.% dry, ash, catalyst-free basis) from catalytic pyrolysis of SAQ lignin

Compound	No catalyst	Al_2O_3	Ni-Al_2O_3-SiO_2	NiO	CaO	CuO	Fe_2O_3	MgO	MoO_3	ZnO	NaOH	KOH	TiO_2
Syringol-type													
Syringol	0.28	0.37	0.42	0.40	0.55	0.41	0.36	0.43	0.33	0.22	0.62	0.53	0.40
4-methylsyringol	0.23	0.29	0.33	0.31	0.37	0.30	0.28	0.36	0.25	0.18	0.29	0.36	0.29
Acetosyringone	0.12	0.14	0.18	0.17	0.20	0.16	0.11	0.20	0.15	0.10	0.21	0.21	0.15
Sum	**0.64**	**0.81**	**0.93**	**0.87**	**1.13**	**0.86**	**0.75**	**0.99**	**0.73**	**0.50**	**1.12**	**1.10**	**0.83**
Guaiacol-type													
Anisole	0.10	0.14	0.20	0.12	0.16	0.13	0.17	0.16	0.17	0.18	0.13	0.10	0.13
4-methylanisole	0.05	0.06	0.09	0.07	0.09	0.07	0.07	0.07	0.06	0.07	0.08	0.06	0.06
Guaiacol	0.57	0.61	0.76	0.72	1.04	0.75	0.73	0.74	0.62	0.48	1.10	0.78	0.68
creosol	0.33	0.39	0.48	0.42	0.55	0.42	0.41	0.46	0.36	0.27	0.41	0.42	0.40
4-ethylguaiacol	0.16	0.20	0.26	0.23	0.29	0.24	0.25	0.24	0.21	0.16	0.28	0.25	0.25
4-vinylguaiacol	0.74	0.80	1.03	0.78	1.36	0.70	0.80	1.11	0.63	0.66	1.17	1.10	0.63
3-methoxycatechol	0.27	0.33	0.38	0.32	0.28	0.28	0.27	0.36	0.28	0.24	0.37	0.38	0.31
Isoeugenol	0.21	0.20	0.20	0.20	0.22	0.19	0.20	0.21	0.19	0.20	0.21	0.21	0.19
Vanillin	0.06	0.08	0.10	0.08	0.11	0.08	0.09	0.10	0.05	0.05	0.10	0.10	0.08
Acetoguaiacone	0.07	0.07	0.08	0.07	0.09	0.08	0.08	0.08	0.07	0.06	0.08	0.09	0.07
Sum	**2.56**	**2.88**	**3.57**	**3.01**	**4.19**	**2.94**	**3.07**	**3.53**	**2.63**	**2.37**	**3.94**	**3.49**	**2.79**
Phenol-type													
Phenol	0.73	0.78	0.91	0.81	1.12	0.91	1.01	0.89	0.78	0.67	0.99	0.80	0.87
o-cresol	0.47	0.50	0.49	0.42	0.66	0.53	0.60	0.53	0.42	0.39	0.52	0.41	0.53
p+m-cresol	0.46	0.50	0.59	0.49	0.68	0.56	0.63	0.56	0.52	0.39	0.49	0.45	0.53
2,4-xylenol	0.08	0.08	0.08	0.06	0.10	0.08	0.09	0.08	0.07	0.06	0.07	0.06	0.08
4-ethylphenol	0.22	0.26	0.34	0.30	0.35	0.31	0.33	0.31	0.30	0.21	0.31	0.29	0.33
Sum	**1.95**	**2.12**	**2.42**	**2.09**	**2.91**	**2.39**	**2.67**	**2.38**	**2.09**	**1.73**	**2.38**	**2.00**	**2.33**
Others													
Toluene	0.12	0.13	0.15	0.13	0.16	0.16	0.18	0.14	0.23	0.10	0.14	0.12	0.14
Furfural	4.29	4.87	6.00	7.05	2.62	6.76	6.17	3.57	5.71	3.36	1.51	3.35	7.87
Total phenols	**5.16**	**5.80**	**6.92**	**5.97**	**8.23**	**6.20**	**6.49**	**6.90**	**5.46**	**4.59**	**7.45**	**6.60**	**5.96**

Table 6-5: Yields of monomeric products (wt.% dry, ash, catalyst-free basis) from catalytic pyrolysis of SEH lignin

Compounds	No catalyst	Al_2O_3	Ni-Al_2O_3-SiO_2	NiO	CaO	CuO	Fe_2O_3	MgO	MoO_3	ZnO	NaOH	KOH	TiO_2
Syringol-type													
Syringol	0.43	0.44	0.47	0.48	0.48	0.53	0.61	0.43	0.55	0.31	0.74	0.64	0.57
4-methylsyringol	0.28	0.30	0.34	0.32	0.31	0.35	0.42	0.31	0.48	0.24	0.19	0.17	0.34
4-allylsyringol	0.04	0.04	0.04	0.04	0.04	0.05	0.05	0.04	0.05	0.03	0.03	0.03	0.04
Acetosyringone	0.06	0.06	0.07	0.06	0.07	0.08	0.08	0.06	0.09	0.05	0.06	0.05	0.07
Sum	**0.80**	**0.84**	**0.93**	**0.90**	**0.89**	**1.01**	**1.16**	**0.84**	**1.16**	**0.64**	**1.02**	**0.89**	**1.02**
Guaiacol-type													
Anisole	0.10	0.12	0.13	0.12	0.17	0.13	0.18	0.17	0.21	0.19	0.15	0.13	0.12
4-methylanisole	0.11	0.11	0.13	0.12	0.17	0.13	0.17	0.16	0.13	0.15	0.18	0.17	0.13
Guaiacol	0.77	0.78	0.85	0.86	0.96	0.94	1.11	0.81	0.95	0.62	1.36	1.23	0.95
creosol	0.34	0.36	0.39	0.38	0.41	0.43	0.49	0.37	0.56	0.30	0.22	0.20	0.45
4-ethylguaiacol	0.11	0.10	0.10	0.10	0.11	0.11	0.13	0.10	0.12	0.09	0.12	0.10	0.11
4-vinylguaiacol	1.33	1.48	1.46	1.50	1.75	1.66	2.00	1.63	2.01	1.36	1.53	1.33	1.62
Isoeugenol	0.25	0.31	0.26	0.25	0.26	0.27	0.28	0.26	0.27	0.24	0.24	0.23	0.25
Vanillin	0.04	0.08	0.05	0.05	0.06	0.06	0.06	0.05	0.07	0.05	0.04	0.04	0.05
Acetoguaiacone	0.06	0.06	0.06	0.06	0.07	0.07	0.07	0.07	0.08	0.06	0.06	0.05	0.06
Sum	**3.10**	**3.40**	**3.43**	**3.43**	**3.95**	**3.79**	**4.51**	**3.61**	**4.42**	**3.06**	**3.90**	**3.47**	**3.74**
Phenol-type													
Phenol	0.87	0.85	0.87	0.89	1.12	0.94	1.22	0.98	1.04	0.81	1.38	1.27	1.01
o-cresol	0.46	0.41	0.38	0.42	0.57	0.44	0.59	0.50	0.48	0.41	0.75	0.62	0.53
p+m-cresol	0.56	0.56	0.47	0.52	0.72	0.61	0.84	0.65	0.88	0.57	0.53	0.42	0.61
2,4-xylenol	0.08	0.07	0.05	0.06	0.10	0.07	0.11	0.09	0.10	0.08	0.10	0.07	0.08
4-ethylphenol	0.15	0.15	0.13	0.14	0.17	0.16	0.20	0.16	0.20	0.14	0.16	0.13	0.16
Sum	**2.13**	**2.05**	**1.91**	**2.03**	**2.68**	**2.22**	**2.96**	**2.38**	**2.71**	**2.02**	**2.92**	**2.52**	**2.38**
Others													
Toluene	0.22	0.27	0.23	0.24	0.31	0.25	0.36	0.28	0.56	0.22	0.31	0.26	0.25
Furfural	0.20	0.16	0.22	0.24	0.22	0.26	0.30	0.24	0.37	0.25	0.15	0.14	0.25
Total phenols	**6.03**	**6.28**	**6.27**	**6.37**	**7.53**	**7.02**	**8.63**	**6.83**	**8.29**	**5.72**	**7.84**	**6.88**	**7.15**

6.4.0. Conclusion

In this study, the production of phenols from three sugarcane bagasse lignins with impregnated catalysts was investigated by screening twelve catalysts based on 1 wt.% content using TGA-TD-GC-MS. The TGA results showed that the dTG curves and

char yields were influenced by the presence of the catalysts meaning modification in mechanisms. The most significant increases in the total yields of phenols were obtained with KOH for SD lignin (25.7 %), CaO for SAQ lignin (59.7 %), and Fe_2O_3 for SEH lignin (43 %). The enhancement of depolymerisation at relatively low temperatures (< 350 ^oC) resulted in the increase of the production of some S-type, and G-type such as syringol, guaiacol, and vinylguaiacol up to 121%, 93%, and 84% respectively. These significant increases in the amounts of phenols produced with low catalyst content of 1 wt.% compared to ≥ 10 wt.% reported in literatures demonstrate the effectiveness of impregnation method.

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6.5. References

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CHAPTER SEVEN

OPTIMISATION OF PHENOLS PRODUCTION FROM CATALYTIC PYROLYSIS OF SUGARCANE BAGASSE LIGNIN

A paper in preparation for submission to *Bioresource Technology*

Titled "Optimisation of phenols production from catalytic pyrolysis of sugarcane bagasse lignin using potassium hydroxide"

Authors: David Naron, François-Xavier Collard, Luvuyo Tyhoda, and Johann. F. Görgens

Objective of dissertation and summary of findings in present chapter

This chapter addresses **objective 4**, to investigate the effects of temperature and catalyst amounts on the production of phenolic chemical products from soda lignin. Study of the conversion of soda sugar cane bagasse lignin in chapter 5 showed that soda lignin catalysed by KOH produced the highest yield (11.3 wt.%) of monomeric phenols when compared to the ones obtained from *E. grandis* and pine lignins (5.4-6.0 wt.%). Also, the conversion of soda lignin catalysed by KOH produced the highest yield of total monomeric phenols (11.3 wt.%) when compared to the conversion of two other sugarcane bagasse lignins namely soda-anthraquinone (maximum yield of 8.2 wt.%), and steam explosion combined with enzymatic hydrolysis (maximum yield of 8.6 wt.%), Hence, soda lignin with KOH was selected for process optimisation to maximise the yields of phenols production.

Firstly, the pyrolysis of soda lignin with KOH was conducted at analytical scale (milligrams) to assess the influence of the catalyst content. The highest yield of total monomeric phenols (15.3-16.0 wt.%) was obtained with catalyst contents within the range of 5-7 wt.% KOH, which was about 74-81% increase compared to non-catalysed conditions. Secondly, the effect of catalyst content and temperature during fast pyrolysis was

investigated at bench scale (gram-scale). The highest yield of total phenols was 3.6 wt.%, of which the maximum was obtained at 450 ^{o}C with 4.5 wt.% and 8.5 wt.% of KOH contents. Syringol, guaiacol, and phenols were the main compounds produced in significant amounts, with absolute yields of 0.71 wt.%, 0.62 wt.%, and 0.96 wt.%, equivalent to 106%, 85%, and 141% increases respectively, as compared to the non-catalytic yields. These yields were significantly lower than the ones obtained at analytical scale, probably due to differences in reactor configuration, and promotion of repolymerisation reactions.

Candidates Declaration

With regards to chapter 7, page numbers 219 to 252 of this dissertation, the nature and scope of my contribution were as follows.

Nature of contribution	**Extent of contribution (%)**
Planning of the experiments	60
Execution of the experiments	100
Interpretation of the results	60
Writing the chapter	100

The following co-authors have contributed to Chapter 7 pages numbers 219 to 252 of this dissertation as follows:

Name	e-mail address	Nature of contribution	Extent of contribution (%)
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		Reviewing the chapter	40
		Interpretation of results to correlate with literature	20
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		Interpretation of results to correlate with literature	10

Signature of candidate…….

Date…….

Declaration by co-authors

The undersigned hereby confirm that the declaration above accurately reflects the nature and extent of contributions of the candidates and co-authors to chapter 7 pages number 219 to 252

in the dissertation no other authors contributed to chapter 7 pages number 219 to 252 in the dissertation besides those specified above, and potential conflicts of interest have been revealed to all interested parties and that are necessary arrangements have been made to use the material in to chapter 7, page numbers 219 to 252 of this dissertation.

Signature	Institutional affiliation	Date

Abstract

Pyrolysis of soda (SD) lignin catalysed by KOH was investigated first at analytical (milligram) scale using TGA-TD-GC-MS to assess the influence of catalyst content on the yields of phenols. Based on the results obtained, fast pyrolysis was then conducted at bench (gram) scale, focussing on the effects of catalyst amounts and temperatures (450-550 ^{o}C) to determine the optimum conditions. The results at analytical scale showed that the amounts of KOH required to maximise the yield of phenols (15.3-16.0 wt.%) were in the range of 5-7 wt.%. Analysis of the bio-oil obtained from a scale up using bench-scale pyrolysis at different conditions showed that the yields of syringol and guaiacol had their maximum values at 450 ^{o}C and 4.5 wt.% KOH content with yield increases of 0.70 wt.% and 0.6 wt.%, which represent 106% and 83% respectively, compared with that of pyrolysis without catalyst. Phenol (the P-type phenol) achieved a maximum at 450 ^{o}C and 8.5 wt.% KOH content, with a yield of 0.96 wt.%, corresponding to 141% increase. Overall, the production of phenols from SD lignin pyrolysis required low temperature (450 ^{o}C) and KOH content (4.5 wt.%), except for the P-type phenols which required a higher KOH content (8.5 wt.%), possibly due to the promotion of demethoxylation reactions. Fast pyrolysis yields at bench scale were found to be significantly lower than slow pyrolysis yields using TGA due to differences in reactor configuration and enhancement of repolymerization reactions.

Keywords: lignin, catalytic pyrolysis, optimisation, phenols

7.1 Introduction

The depletion of fossil fuels and their adverse effects on the environment have prompted interest in the exploration of alternatives that are renewable [1]. Recently, attention has been shifted to lignocellulosic biomass as an alternative renewable

source that can be transformed into fuels and chemicals, because it is widely produced in nature, sustainable, relatively cheap, and is not in conflict for food supply [2,3]. Lignocellulosic biomass is made up of three major components which are cellulose, hemicelluloses and lignin. Lignin is the second most abundant natural polymer after cellulose. Interest in lignin has increased in recent time due to its aromatic nature, seen as an opportunity to produce value-added chemical products [1,4].

Lignin can be valorised by pyrolysis, in which the bio-oil, as one of the major products contains numerous monomeric phenols [5,6]. Phenolic compounds are platform chemicals known to have wide applications in the fields of medicines, cosmetics, adhesives etc [7–9]. The proportions of phenolic compounds in the lignin-derived bio-oil will depend on several process variables, particularly reaction temperature, reactor type, residence time of volatiles, catalyst, heating rate, and lignin source [10,11]. Previous studies have found that temperature has major influence on the chemical product distributions, and this parameter has been widely investigated [12–14]. However, the relatively low yields of generated products, mostly less than 10 wt.% [15], and non-selectivity to the desired chemical products have prompted researchers to further investigate other factors.

Of recent, several researchers have focussed on the investigation of the effect of catalyst to improve the yields and selectivity of the desired chemical products from lignin pyrolysis. In chemical (non-pyrolytic) approaches such as reductive catalytic fractionation, lignin monomeric products are obtained by fractionation of the whole biomass. In this approach, fractionation of lignocellulosic biomass is performed in the presence of reduction catalysts such as Pd, Ni, Ru etc. and hydrogen donor agents such as methanol, isopropyl alcohol, formic acid etc [16–18]. This approach has yielded high yields of phenols monomeric products up to 50 wt.% or more, due to

stabilisation of the monomeric phenols by the hydrogen-donating agents [18]. However, the process is complicated, plagued by numerous problems that are related to product contamination, product recovery, use of harsh reaction conditions such as the use of high pressures in the presence of hydrogen gases, making the process hardly viable [18].

With pyrolysis, although yields reported so far from isolated lignin have been lower, within the range of 5-37 wt.% [7,14,19,20], compared to RCF, pyrolysis is cheaper and easier to implement [4], and the generated products are relatively evenly distributed [4,5]. Hence, several researchers have focused on catalytic pyrolysis of lignin to phenolic products. For example, Peng et al. [21], studied the pyrolysis of alkali and purified lignins physically mixed with 0-20 wt.% of alkaline additives using a fixed bed pyrolysis reactor at 450 ^{o}C. The aim was to understand the pyrolysis behaviours of the two lignins towards the production of phenols. The maximum bio-oil yield obtained was 30 wt.%, estimated to contain 80 % of phenolic products. However, the yields of phenolic compounds identified from the bio-oil were not provided. Nair and Vinu. [7] performed fast pyrolysis of alkali softwood lignin physically mixed with synthesised TiO_2, ZrO_2, and CeO_2 catalysts using a micropyrolyser operated at 500 ^{o}C. Their main interest was in the production of guaiacol-related phenols. They found that a maximum yield of phenols (about 37 wt.% based on internal calibration) was produced from lignin catalysed by TiO_2. Mate et al. [20] studied the selectivity of two titanium oxides (anatase and rutile) towards the production of lower molecular weight phenols. At the temperature of 550 ^{o}C and a catalyst-to-feed ratio of 5 wt.%, the yields of simple phenols (cresol, phenol, and xylenol) were maximised, with anatase as the most effective catalyst. Guo et al. [22] studied the effect of chemical form of sodium on the product characteristics of alkali

lignin. They found that the organic bound sodium increased the yields of guaiacol and phenol by the removal of alkyl substituents, while inorganic sodium enhanced the formation of ethers by the removal of phenolic hydroxyl groups. However, the yields of the phenolic compounds were not quantified.

From these previous reports, it is clear that the preferred pyrolysis reaction temperatures and catalyst contents to maximise the yields of phenolic compounds from lignin, are to be determine empirically. The few that focussed on the study of the effects of temperature and catalyst contents on the pyrolysis of lignin to produce phenols either do not quantify the phenols or estimate the phenols yields based on comparison of total chromatographic peak area values, which are not the exact mass yields of the phenolic compounds [23]. Furthermore, while in most of the studies the catalysts were physically mixed with the lignin, the adoption of impregnation method will foster close interactions between the catalyst and the lignin, and thereby promote a better catalytic role for the conversion of the lignin [24].

Therefore, this study aimed to investigate the influence of temperature and (impregnated) catalyst (KOH) content on the yields of phenolic compounds from the pyrolysis of soda lignin. The choice of soda lignin with KOH catalyst was informed by the relatively high yield of phenolic compounds obtained in a previous work (chapters 5 and 6). The soda lignin was impregnated with different amounts of KOH and pyrolysis optimisation was conducted in two stages. The first stage was conducted using analytical pyrolysis technique at milligram-scale, while the second stage was conducted using a bench-scale pyrolyser, using gram-quantities of lignin. The analytical pyrolysis experiments were performed using thermogravimetric analysis (TGA) at 600 ^{o}C using a heating rate of 10 ^{o}C/min, and the TGA-TD-GC-MS method. The analytical pyrolysis experiments served as a guide to select the range of

catalyst contents. Bench-scale fast pyrolysis experiments were then conducted using a batch induction-heating coil reactor. Fast pyrolysis was considered as it is known to generate much higher bio-oil yield than slow pyrolysis [25]. At bench scale, the effect of pyrolysis temperature and catalyst content on the yields of phenolic compounds were optimised. The bio-oil generated was analysed using GC-MS to quantify the monomeric phenolic compounds present.

7.2. Experimental

7.2.1. Materials

The soda (SD) lignin investigated in this study was extracted from sugarcane bagasse black liquor sample collected from a pulping process in South Africa. The characteristics of this lignin has been reported in our previous work [26]. In summary, the content of C, H, S, and N were 61.2%, 5.5%, 0.2% and 2.9% respectively. The proximate analysis of the soda lignin on dry basis was 66.7 wt.% volatile, 29.6 wt.% fixed carbon and 4.5 wt.% ash. The residual sugars present was 6.4 wt.%. Potassium hydroxide (KOH), with purity of about 98%, purchased from Edutrade, was selected for the catalytic pyrolysis of the soda lignin, due to its good performance with soda lignin. The phenols standards used in this study included 2,6-dimethylphenol, acetosyringoneuaiacol, 4-ethylguaiacol, 4-vinylguaiacol, eugenol, syringol, 4-methylsyringol, allylsyringol, 4-propylguaiacol, trans-isoeugenol, isoeugenol, vanillin, acetoguaiacone, toluene, 3-methoxycatechol, phenol, o-cresol, p+m cresol, creosol, anisole, 4-methylanisole, 3-hydroxy-4-methoxyacetophenone, ethenylanisole, 2,4-xylenol, catechol, 4-ethylphenol, and furfural. They were all analytical grades purchased from Sigma-Aldrich and were used as received.

7.2.2. Lignin impregnation with KOH

Before the analytical catalytic pyrolysis experiments in the TGA, the lignin sample was impregnated with different contents of KOH, with amounts equivalent to 1 wt.%, 3 wt.%, 5 wt.%, 7 wt.%, and 10 wt.% of the lignin mass. The lignin-catalyst mixtures were placed in 150 ml Scott bottles followed by the addition of 20 ml of distilled water. The mixtures were stirred with a Velp Scientifica multiple stirring system set at 300 rpm at ambient temperature for 24 h. After complete homogenisation, the water from the solutions were evaporated using magnetic stirring hotplates set at 100 rpm and heated from ambient temperatures to 80^{o}C until resistive movements of the magnets were reached. The magnets were removed from the slurry samples and then dried for 24 h in the oven set at 100 ^{o}C. The sizes of the dried samples were reduced to particle sizes of ≤ 425 µm and then stored in zipped bags before the pyrolysis experiments.

7.2.3. Analytical pyrolysis experiments using TGA-TD-GC-MS

Thermogravimetric analyser (Mettler Toledo TGA/DSC 1-LF1100) system was used to carry out pyrolysis of the lignin samples (approximately 10 mg) at a heating rate of 10 ^{o}C/min heating from ambient temperatures to 600 ^{o}C in an argon flow of 70 mL/min. The volatiles released from the TGA were captured into thermal desorption (TD) tubes and analysed using an Agilent Technology 7890A GC via a Unity 2 desorption system heated to 300 ^{o}C (maintained for 10 min). Helium gas flowing at the rate of 10 mL/min and a split flow of 97 mL/min was used to facilitate both volatile removal from the TD tubes and transfer into the GC-MS line. Separation of the volatiles was achieved using ZB-1701 (60 m x 0.25 mm x 0.25 µm-Agilent Technologies) capillary column with a chemical composition of 14%

cyanopropylphenyl-methylpolysiloxane. The temperature programme of the GC oven began at 45 ^{o}C (10 min) followed by a heating rate of 2 ^{o}C/min to 100 ^{o}C, and 7 ^{o}C/min to 260 ^{o}C for 14 min. The electron impact (EI) mass spectra were obtained by Agilent mass spectrometer (MS) at 70 eV, and the mass ranged from m/z 20-500. Phenol calibration on the GC-MS was done by injection of a mixture of 29 standard compounds of known concentration, diluted with an ACS grade acetone (purity >99.9%) purchased from Sigma Aldrich. Calibration curves were made by injecting 3 µL of the standard solution and 3 µL of internal standard following the same TD-GC-MS method. The compounds from chromatograms were identified by NIST 2011 mass spectrometer library, and by comparison of the retention time with those of the standard compounds. Reproducibility and accuracy of the data were ensured by conducting all the experiments at least in duplicates. Acceptable variability in the phenols yields was 15% relative standard deviation (RSD).

7.2.4. Bench-scale fast pyrolysis with induction coil pyrolyser

7.2.4.1. Experimental Design

A 3^2 factorial experimental design was employed in the catalytic pyrolysis process at the bench-scale. The selected independent variables were reaction temperature and catalyst content. The selected range of temperatures were 450 ^{o}C, 500 ^{o}C and 550 ^{o}C, while those of the catalyst contents were 4.5 wt.%, 6.5 wt.%, and 8.5 wt.%, representing the lower, middle and upper values of the experimental design respectively. The selected dependent variables were the yields of bio-oil, bio-char, bio-gas and total monomeric phenols. The detail of the experimental design and the yield distribution is presented in Table 7-2.

7.2.4.2. Fast pyrolysis experiments

After the TGA-TD-GC-MS experiments, fast pyrolysis experiments were performed using a horizontal externally heated fixed reactor with a length of 45 cm and an internal diameter of 10 cm, heated by induction-heating coils, which is shown schematically in Figure 7-1. The fixed bed pyrolyser allows the pyrolysis of a larger amount of sample than the TGA. Briefly, about 10 g of dried lignin obtained by wet impregnation of the lignin with catalyst, in amounts equivalent to 4.5 wt.%, 6.5 wt.%, and 8.5 wt.% of the lignin mass were placed into a pyrex glass crucible and then housed in the middle of the fixed bed reactor, and then pyrolysed at different temperatures of 450 ^{o}C, 500 ^{o}C and 550 ^{o}C. Before the start of the experiments, the reactor was purged with nitrogen, as the carrier gas, flowing at the rate of 2.5 L/min for 30 min to achieve an inert atmosphere. Lignin samples were heated from room temperature to the desired temperature at a heating rated of 250 ^{o}C/min, and then maintained at the desired setpoint for 30 min. Cooling water maintained at 7 ^{o}C, flowing through the condensers and the reactor surrounding was used to condense the pyrolysis volatiles. The resulting bio-oil collected in the atmospheric pot, condensers, electrostatic precipitator (ESP) and connecter were recovered by washing with analytical grade acetone (purity >99.99%). The bio-oil mixed with acetone was stored in the dark at 5 ^{o}C before analysis on the GC. The pyro-gases were collected with 5 L Tedlar bags, approximately every 2 min and immediately analysed offline using a micro GC. The char was recovered and weighed after the reactor cooled down to room temperature under nitrogen. To ensure that correct mass balances were achieved, all parts of the reactor system were weighed before and after the experiments. Also, reproducibility of the procedure was ensured by conducting the experiments at least two times.

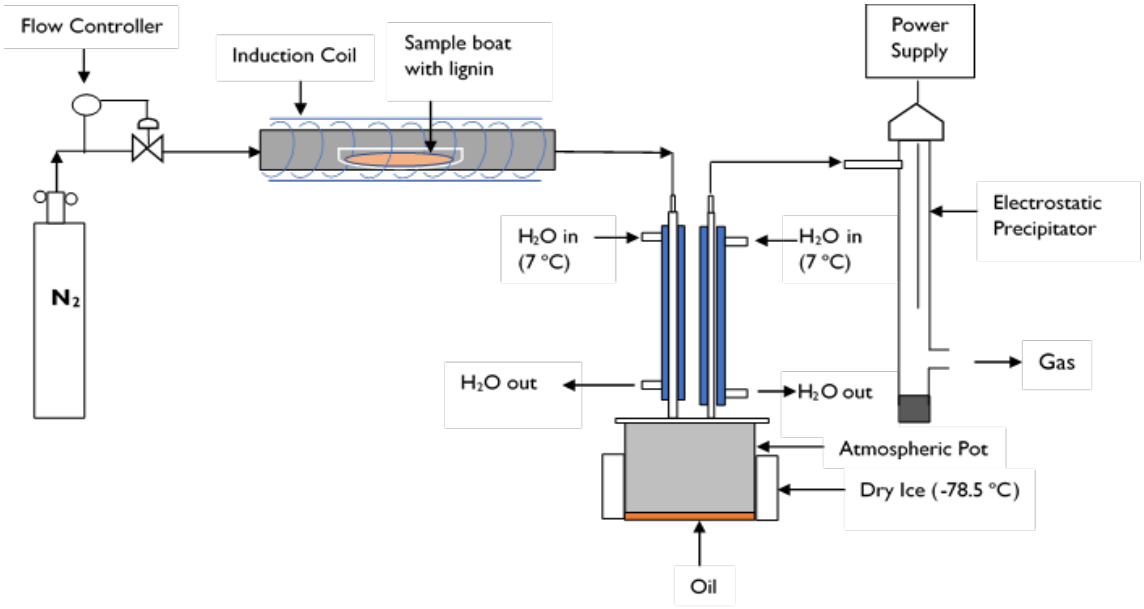

Figure 7-1. Schematic diagram of the fast pyrolysis system

7.2.4.3. Characterisation of bio-oil

7.2.4.3.1. GC-MS analysis of bio-oil

GC-MS analysis of the bio-oil obtained after fast pyrolysis experiments were performed on an Agilent 7890A GC equipped with an Agilent Technologies 5975C MS. Before the analysis, the bio-oil was placed in a 50 mL flask and diluted to the mark with analytical grade acetone (purity >99.9%), and then filtered through a 0.45 µm micro filter. Thereafter, 1 mL of the filtered sample was mixed with 1 mL of 2-octanol (0.1 g/L) used as internal standard and then injected (1 µL) into the GC column with auto-sampler. The GC column used was a 60 m x 0.25 mm i.d. x 0.25 µm film thickness model ZB-1701 (14% cyanopropylphenyl-methylpolysiloxane) Agilent Technologies. Injection was performed in a split mode with a split ratio of 20:1. The temperature programme adopted was as follows: oven temperature started at 45 ^{o}C for 10 min, and then increased to 260 ^{o}C at the rate of 7 ^{o}C/min. The carrier gas was helium (purity >99.9%). The MS was operated in EI mode and the mass

spectra were obtained in the mass to charge (m/z) range of 20-500 with an ion source of electron impact at 70 eV. Calibration of phenols was done by injecting standard mixture containing 29 compounds into the GC-MS. Identification of targeted phenols was achieved according to NIST 2011 MS library and by comparing the retention time with those of the standard compounds.

7.2.4.3.2. Gas composition analysis

The non-condensable gas components, mainly CO, CO_2 and CH_4, C_2H_6, C_2H_4, C_3H_8, and C_3H_6 collected with 5 L Tedlar bags at 2 min intervals were analysed using a Compact Gas Chromatograph set-up (CompactGC 4.0). The carrier gases used were argon and helium (baseline 5.0 Afrox). Before quantification, the Compact GC was calibrated with known concentration of all the gas species. The mass of each gaseous product produced during pyrolysis was calculated based on the knowledge of the total volume of nitrogen flowing during pyrolysis and the accumulated amount collected in the sampling bags.

7.3. Results and Discussion

7.3.1. TGA pyrolysis soda lignin with different KOH contents

Analytical pyrolysis was performed with soda sugarcane lignin using the TGA-TD-GC-MS method, at a heating rate of 10 ^{o}C/min up to 600 ^{o}C. The TG and DTG curves for the lignin pyrolysis without catalysts and with the various contents of KOH are shown in Figure 7-1a-b. During lignin pyrolysis without catalyst the mass loss occurred over a wide range of temperature (150 ^{o}C to 600 ^{o}C) and was comprised of two major decomposition stages. The first decomposition stage with a maximum at temperature of 272 ^{o}C was attributed partly to decomposition of hemicellulose impurities and lignin. Given that the sugar content (6.4 wt.%) was lower than the mass loss (15%) corresponding to the peak (Figure 7-1a), significant conversion of

lignin on this temperature range was clear. The second decomposition stage, with a peak at the temperature of 376 ^{o}C (Figure 7-1b), corresponding to the maximum degradation rate, was ascribed to the decomposition of the main structure of lignin, as reported previously [27–29]. The final char yield generated from the lignin pyrolysis without catalyst was 35.2 wt.%.

In the presence of the various contents of KOH as catalyst, changes in the pyrolysis curves were observed, which evidenced modifications to mechanisms of mass losses. Only for the lignin catalysed by 1 wt.% of KOH content, the DTG curve was also composed of two peaks, with the first one observed at higher temperature (307 ^{o}C) with corresponding mass loss of 19%, similar to uncatalysed. With the remaining catalyst amounts (3 wt.%, 5 wt.%, 7 wt.% and 10 wt.%) only one DTG peak was observed, with maximum degradation rates in the range of 291-309 ^{o}C. The temperatures corresponding to the maximum decomposition rates shifted to lower values with increasing catalyst content, 291 ^{o}C (10 wt.%) < 293 ^{o}C (7 wt.%) < 300 ^{o}C (5 wt.%) < 309 ^{o}C (3 wt.%) < 364 ^{o}C (1 wt.%). The temperature reduction phenomenon involving alkali salts has previously been reported in literatures [30–32]. Three possible roles (catalytic role during pyrolysis, swelling role during impregnation, or both roles) displayed by the alkali (KOH) catalyst, could be responsible for the occurrence of these effects [32].

The char yields (expressed on dry, ash, catalyst-free basis) obtained with the various KOH contents were much higher than that without catalyst (35.2 wt.%) and were proportionally increased with increases in the KOH content. The order of increase followed the trend: 35.8 wt.% (1 wt.%) < 40.5 wt.% (3 wt.%) < 42.1 wt.% (5 wt.%) < 43.1 wt.% (7 wt.%) < 43.4 wt.% (10 wt.%). This trend was attributed to some volatile recombination at the catalyst surface, resulting in secondary char formation [31].

Furthermore, char promotion during pyrolysis is characteristic of alkali salts, and have been reported in several literatures [21,31,32].

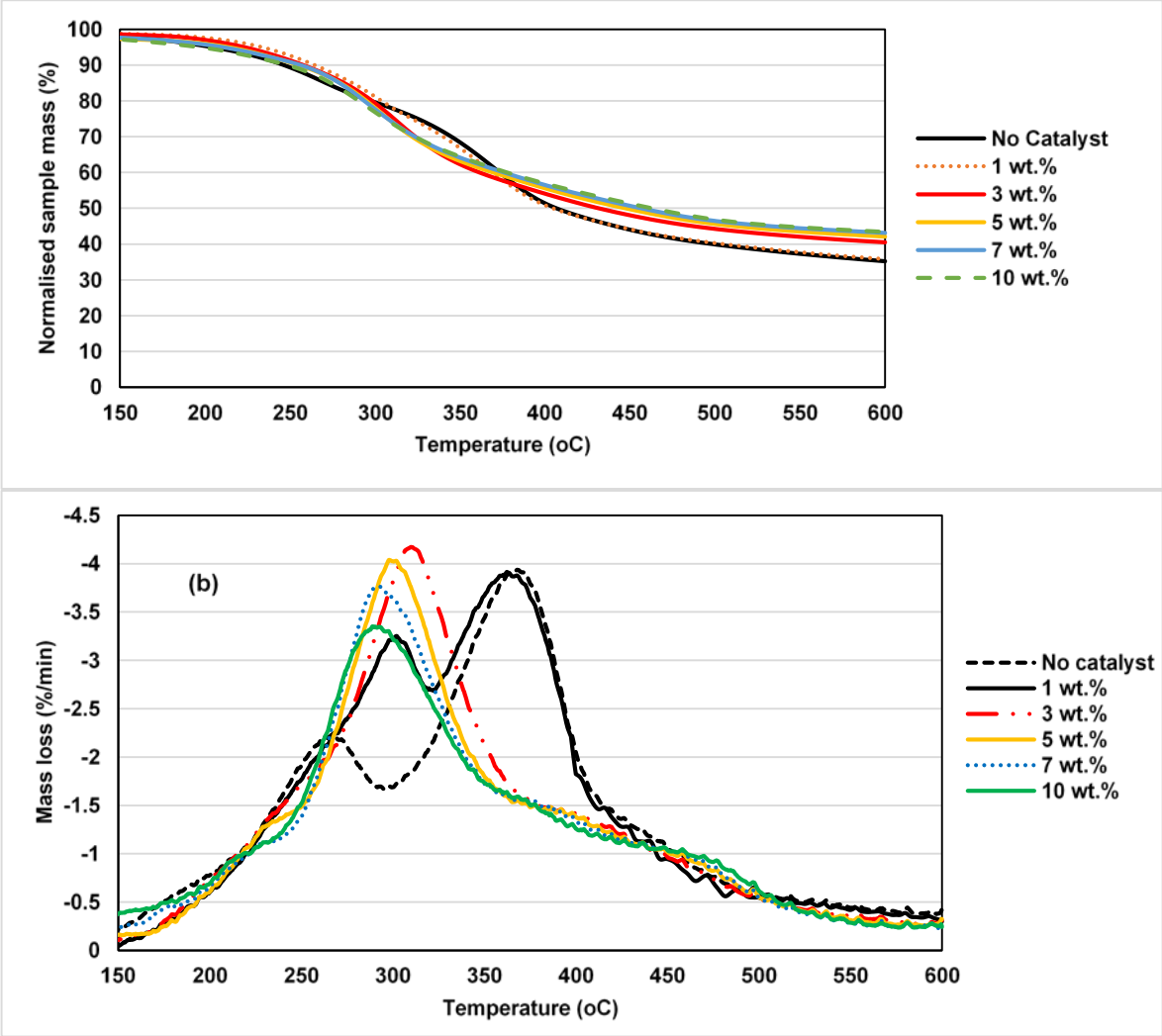

Figure 7-2a-b: TG curves (a) and DTG curves (b) of soda lignin pyrolysed without catalyst and with various KOH contents at a heating rate of 10 ºC/min

7.3.2. Effect of KOH contents on phenols from pyrolysis using TGA-TD-GC-MS

Table 7-1 presents the yields of phenolic compounds obtained from catalysed lignin pyrolysis using TGA-TD-GC-MS. After the application of the various KOH contents, the compositions and yields of the phenolic products were altered significantly. To show the changes of the product composition, the identified phenolic compounds

were divided into three categories as syringol-type (S-type), guaiacol-type (G-type), and phenol type (P-type) phenols, and the result is shown in Table 7-4. Figure 7-3 represents the yields of each phenol type obtained with and without catalyst (1 wt.%, 3 wt.%, 5 wt.%, 7 wt.%, and 10 wt.%). From Table 7-1, it is seen that the total phenols yields were all increased from 8.8 ± 2.1 wt.% without catalyst, to between 9.0-16.0 wt.% with catalyst. The yields generally increased as the KOH content increased, except for the highest content of KOH (10 wt.%), where a decrease was observed (Table 7-1). At 5 wt.% and 7 wt.% KOH contents, the phenols yield attained the maximum values of 15.3 ± 0.2 wt.% and 16.0 ± 2.2 wt.% respectively, equivalent to 74% and 81% increases respectively, as compared to the non-catalytic yield (Table 7-1). Compared with literature, Nair and Vinu, [7] reported a slightly higher total phenols yield increase of 106% when converting softwood alkali lignin in the presence of 10 wt.% content of TiO_2 catalyst.

In terms of phenols groups as S-type, G-type, and P-type phenols, the relative contents obtained for the pyrolysis of SD lignin without catalyst reflected the fact that it is a non-woody lignin, which is usually composed of syringyl/guaiacyl/hydroxyphenyl (S/G/H)-units. The G-type compounds were the dominant products, accounting for about 49%, ascribed to its basic structure, which is mostly composed of guaiacol propane [29].

For the catalytic pyrolysis, from Figure 7-2, the influence of the various KOH contents shows that the yields of S-type decreased by 41% with 10 wt.% KOH content. Similarly, the yields of G-type phenols increased from 4.4 wt.% to between 5.8-6.4 wt.%), and then decreased to 3.4 wt.% at 10 wt.% KOH content. The decrease at the 10 wt.% KOH content for both S-type and G-type phenols suggested that demethoxylation reactions were enhanced [33]. Syringol, guaiacol and 4-

vinylguauacol were the major S-type and G-type phenols with yields increases within the range of 1.0-2.8 wt.%, as compared to the yields obtained without catalyst (Table 7-1). The highest yields of syringol and guaiacol compounds were obtained with 7 wt.% KOH content (1.41 wt.% and 3.41 wt.%), equivalent to 118% and 238% increases, as compared to 0.65 wt.% and 0.34 wt.% obtained without catalyst respectively. Pyrolysis with 1% wt.% KOH produced the highest yield increase of 4-vinylguaiacol from 1.94 wt.% to 2.79 wt.%, the production which progressively decreased with the increase in KOH content.

Concerning the P-type phenols (Figure 7-2), the presence of catalyst resulted in yield increase at different KOH contents. The yield attained a maximum at 5 wt.% and 7 wt.% KOH content, with yield increase from 3.14 wt.% to 7.47 wt.% and 8.02 wt.%, equivalent to 130% and 147% increases, respectively. The major P-type compound whose yield was increased remarkably was phenol of which 5 wt.% and 7 wt.% KOH content produced the most effects (Table 7-1). The yield of phenol was increased from 1.40 wt.% to 5.23 wt.% and 5.61 wt.%, equivalent to 274% and 301% respectively, which is comparable with the highest yields increases (314-736%) reported in literature [20]. Generally, the increased formation of P-type phenols can be a consequence of the enhancement of lignin depolymerisation and demethoxylation of the S- and G-type phenols [34].

Overall, the maximum yields of phenols from SD lignin lied in the range of 5-7 wt.% KOH contents.

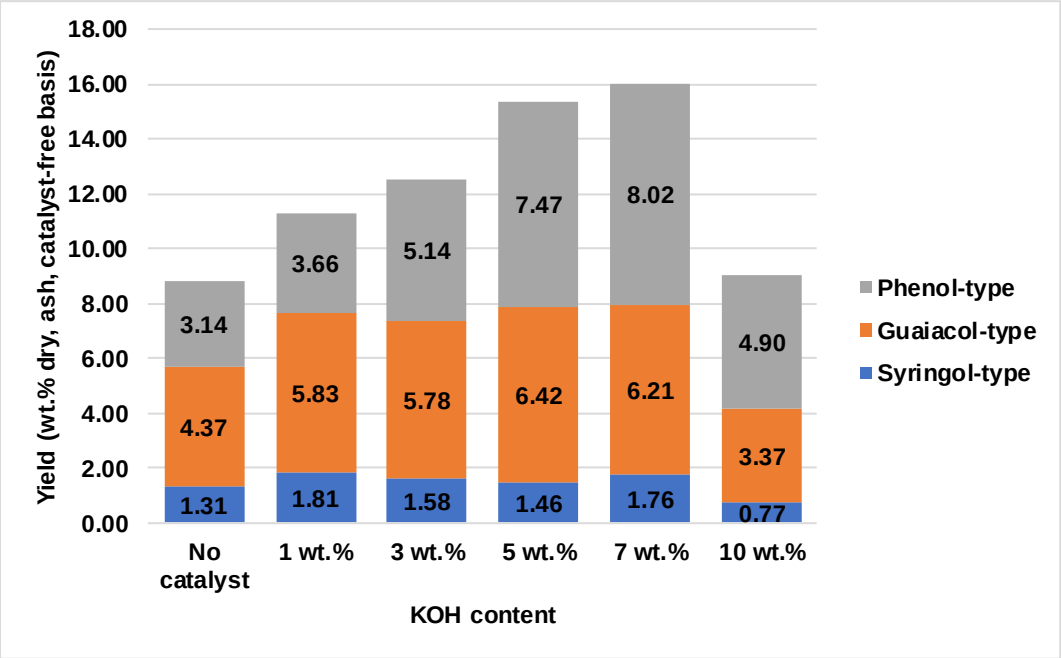

Figure 7-3: Yields of syringol-type, guaiacol-type, and phenol-type compounds from pyrolysis of SD lignin with various KOH contents using TGA-TD-GC/MS

Table 7-1: Yields pf phenols (wt.% dry, ash, catalyst-free basis) obtained from the catalytic pyrolysis of SD lignin using TGA-TD-GC/MS

Compound	No catalyst	1 wt.%	3 wt.%	5 wt.%	7 wt.%	10 wt.%
Syringol-type						
Syringol	0.65	0.96	1.21	1.11	1.41	0.60
4-methylsyringol	0.45	0.58	0.18	0.18	0.16	0.08
4-allylsyringol	0.03	0.06	0.03	0.02	0.02	0.01
Acetosyringone	0.18	0.22	0.17	0.15	0.17	0.07
Sum	**1.31**	**1.81**	**1.58**	**1.46**	**1.76**	**0.77**
Guaiacol-type						
Anisole	0.09	0.10	0.00	0.00	0.00	0.00
4-methylanisole	0.11	0.13	0.22	0.32	0.27	0.19
Guaiacol	1.01	1.40	2.37	3.10	3.41	1.99
creosol	0.63	0.59	0.44	0.46	0.45	0.26
4-ethylguaiacol	0.32	0.32	0.58	0.68	0.84	0.44
4-vinylguaiacol	1.94	2.79	2.01	1.73	1.13	0.43
Isoeugenol	0.13	0.28	0.02	0.00	0.00	0.00
Vanillin	0.08	0.12	0.07	0.07	0.04	0.02
Acetoguaiacone	0.08	0.11	0.07	0.07	0.07	0.04
Sum	**4.37**	**5.83**	**5.78**	**6.42**	**6.21**	**3.37**
Phenol-type						
Phenol	1.40	1.53	3.54	5.23	5.61	3.43
o-cresol	0.54	0.83	0.39	0.64	0.68	0.47
p+m-cresol	0.65	0.78	0.48	0.68	0.65	0.41
2,4-xylenol	0.10	0.12	0.10	0.16	0.20	0.13
4-ethylphenol	0.45	0.40	0.63	0.77	0.87	0.46
Sum	**3.14**	**3.66**	**5.14**	**7.47**	**8.02**	**4.90**
Others						
Toluene	0.24	0.32	0.31	0.57	0.55	0.46
Furfural	2.12	1.56	0.28	0.27	0.00	0.00
Total phenols	**8.82**	**11.31**	**12.50**	**15.34**	**15.98**	**9.03**

7.3.3. Catalytic pyrolysis at bench-scale

According to the results of the analytical pyrolysis method using TGA-TD-GC-MS, the yields of phenols from SD lignin were maximised using the KOH contents

ranging from 5-7 wt.% (Table 7-1). As some differences are expected in terms of mechanism at TGA and bench scale, the range of catalyst content considered for the design of experiment (DoE) at bench scale was 4.5-8.5 wt.%. In addition, the TGA profiles (Figure 7-1a-b) revealed that most of the volatiles were generated at temperature less than 450 ^{o}C, hence, the DoE for the fast pyrolysis was conducted with temperatures within the range of 450-550 ^{o}C (Table 7-2). Maximum bio-oil yields from lignin pyrolysis are generally reported with fast heating rates and temperatures within this range [28,35]. In addition to the test conditions obtained from the DoE, the pyrolysis of lignin was also performed without catalyst at 450 ^{o}C, and 550 ^{o}C. The experiments were conducted at least in duplicate as shown in Table 7-2, and the yields of the three pyrolysis products namely, bio-oil, char, and gas obtained at these conditions are presented in Figure 7-3.

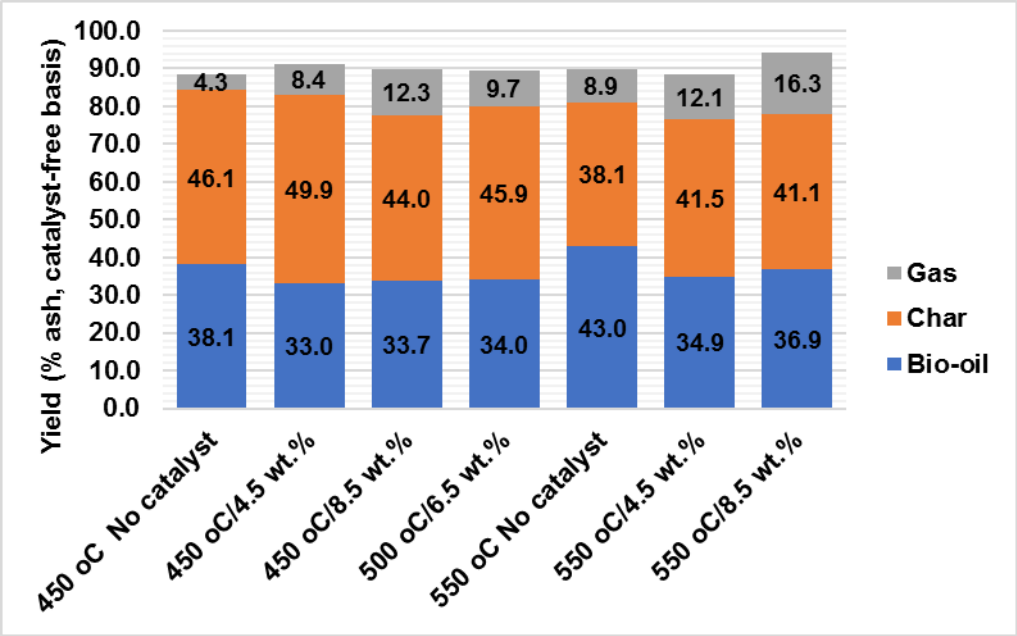

Figure 7-4: Yield of bio-oil, bio-char and bio-gas obtained from the catalytic pyrolysis of soda lignin using bench-scale fast pyrolysis reactor.

The linear model equation obtained from the DoE for the product yields using statistica software version 13.2 is as follows:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2$$

Where y = response variable; the $\beta_{0\text{-}2}$ = model coefficients from statistical analysis; x_1 = temperature, and x_2 = catalyst. A summary of the analysis of variance (ANOVA) for the products yields obtained is shown in Table 7-3. Based on Table 7-3, some p-values less than 0.05 (95% confidents limit) indicate that temperature and catalyst content had significance influence on some of the products yields during pyrolysis. For example, both parameters had significant influence on the yield of gas and char, while only temperature had significant influence on the yields of bio-oil.

Table 7-2: Experiment design including the yield distribution (statistical design only includes the test with catalyst)

Run	Temperature (°C)	Catalyst content (wt.%)	Bio-oil (%)	Char (%)	Gas (%)	Total phenols (wt.%)
1	450	-	40.13	45.03	4.21	2.97
2	450	-	36.07	47.19	4.36	2.69
3	550	-	44.81	36.79	9.45	3.15
4	550	-	41.17	39.38	8.31	2.58
5	450	4.5	32.39	51.11	8.31	3.37
6	450	4.5	33.61	48.71	8.46	3.76
7	450	8.5	33.22	44.10	10.66	3.22
18	450	8.5	34.17	43.81	13.89	3.92
19	500	6.5	33.14	44.51	9.29	3.37
10	500	6.5	34.86	47.32	10.11	2.96
11	550	4.5	36.58	42.09	11.27	2.97
12	550	4.5	33.24	40.90	12.93	3.18
13	550	8.5	36.44	41.20	14.96	3.12
14	550	8.5	37.27	41.09	17.64	3.21

Table 7-3: Statistical results with p-values for bio-oil, gas, char, and total phenols yields and their effects.

Variables	Factor	Coeff. Bio-oil yield	Bio-oil yield P-value	Coeff Char yield	Char yield P-value	Coeff. Gas yield	Gas yield P-value	Coeff. Total phenols yield	Total phenols yield P-value
β_0	Mean/Intercept	34.49	$< 1 \times 10^{-7}$	44.48	$< 1 \times 10^{-7}$	11.74	$< 1 \times 10^{-6}$	3.31	$< 1 \times 10^{-7}$
β_1	Temp (^{o}C) L	1.27	0.028	-2.81	0.0016	1.95	0.025	-0.22	0.067
β_2	Catalyst (wt.%) L	0.66	0.18	-1.58	0.022	2.04	0.021	0.02	0.82
$\beta_1\beta_2$	1 by 2	0.31	0.50	1.40	0.034	0.06	0.93	0.02	0.84

Coeff.: Coefficient, **1 by 2**: interaction function between temperature and catalyst.

7.3.4. Effects of process conditions on products yields distribution

7.3.4.1. Effect of temperature and catalyst content on the bio-oil yield

From Figure 7-4, the pyrolysis of lignin without catalyst at 450 ^{o}C and 550 ^{o}C, produced bio-oil yields of 38.4 ± 2.9% and 43.2 ± 2.6% respectively. The maximum yields of bio-oil obtained from lignin pyrolysis (34-60 wt.%) has been reported at 350-550 ^{o}C [28,35,36].

For the catalytic pyrolysis of SD lignin at different temperatures and KOH contents, temperature was found to have significant influence on the yield of bio-oil, with p-value of 0.03, while catalyst content had no statistically significant influence, with a p-value of 0.20 (Table 7-3). On the studied temperature range, the yields of bio-oil increased with increase in temperature as indicated by the positive factor coefficient (+1.27). For catalyst content between 4.5 and 8.5 wt.%, the coefficient corresponding to catalyst effect was positive, signifying increase in bio-oil yield with increased catalyst content (Table 7-3). However, it was observed that the bio-oil yield decreased by 11-18% on the addition of the various contents of KOH, as compared to the non-catalytic yields (Figure 7-3), consistent with literature report, where the pyrolysis of

lignin with alkali salts resulted in the reduction of the bio-oil yield [21]. From Figure 7-4, illustrating the response surface and contour lines of bio-oil yield as a function of temperature and catalyst content, the major role of temperature can clearly be observed.

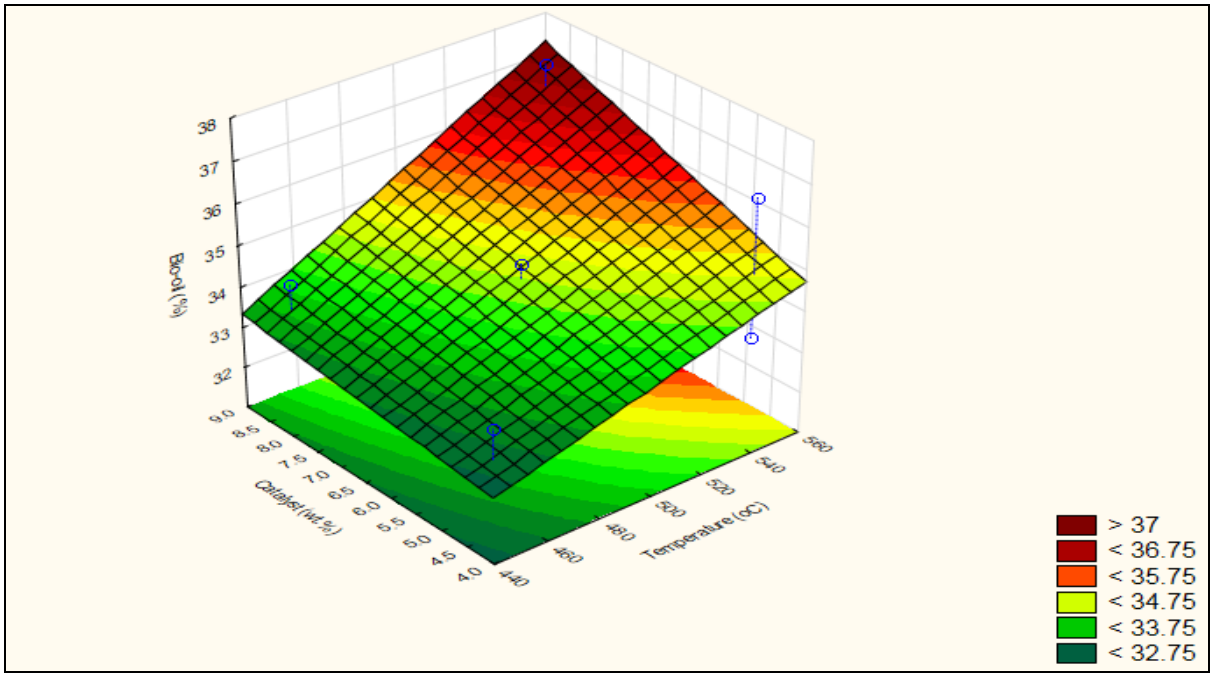

Figure 7-5: The response surface and contour lines of bio-oil yield as a function of temperature and catalyst content

7.3.4.2. Effect of temperature and catalyst content on the gas yield

Both temperature and catalyst content significantly influenced the gas yields from lignin pyrolysis, with p-values of 0.03 and 0.02. The response surface and contour lines of gas yield as a function of temperature and catalyst content is illustrated in Figure 7-5. The yield of gas increased with increase in temperature and KOH content as confirmed by the positive coefficient (+1.94 and +2.02), respectively (Table 7-3). With increase in temperature from 450 ^{o}C to 550 ^{o}C, the increase was attributed to the cleavage of more bond linkages of the phenols substituents [37,38]. With increase in

KOH content gas yields increase was attributed to the catalytic cracking of the phenols substituents. This result is similar to literature report [39], where the presence of inorganic salts in biomass was found to have great influence on the release of gaseous products during pyrolysis. This is due to the lowering of the activation energy of the pyrolytic reactions, enhanced by the presence of the catalyst.

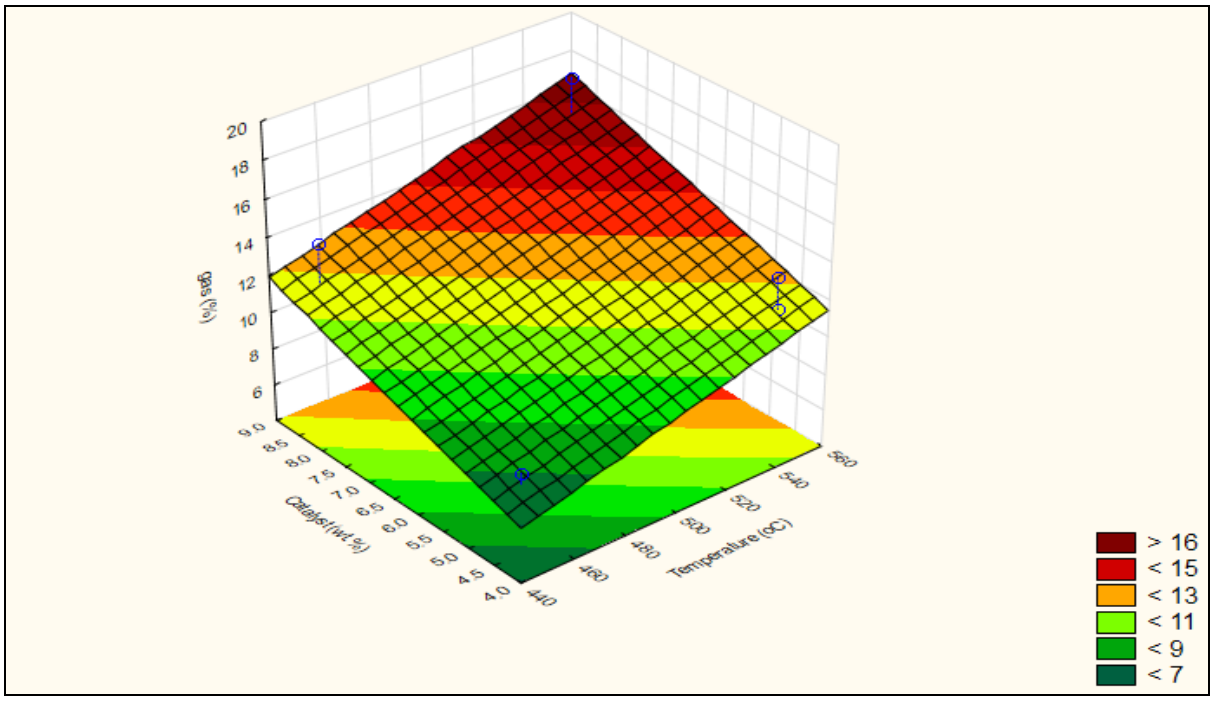

Figure 7-6: The response surface and contour lines of gas yield as a function of temperature and catalyst content

7.3.4.3. Effect of temperature and catalyst content on the char yield

For the char yield, both temperature and catalyst had pronounced influence, with statistical significance p-values of 0.0016 and 0.0022 respectively, (Table 7-3). The yield of char decreased with increase in temperature and catalyst content (Figure 7-4), as indicated by the negative coefficient factors of -2.81 and -1.58 respectively (Table 7-3). However, when compared to the yields of char obtained without catalyst, the addition of the KOH resulted in increase in the yield of char (as observed with the

pyrolysis at analytical scale using TGA-TD-GC-MS (section 3.2)), except for pyrolysis at 450 °C/8.5 wt.% KOH content (Figure 7-4). The influence of temperature and catalyst content on the yield of char is illustrated in Figure 7-6.

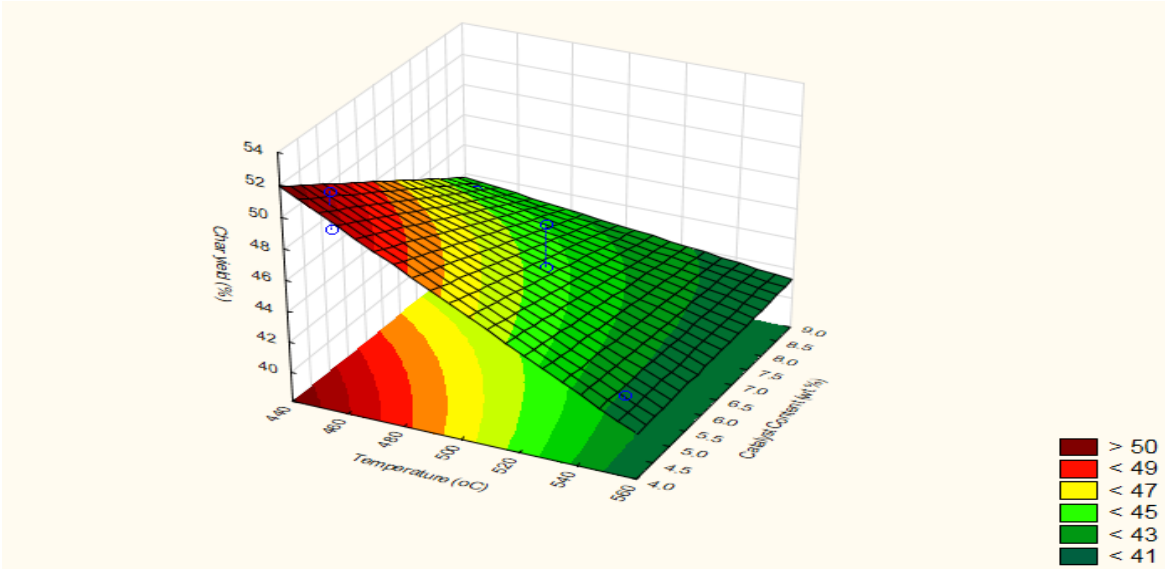

Figure 7-7: The response surface and contour lines of char yield as a function of temperature and catalyst content

7.3.4.4. Effect of temperature and catalyst content on the yield of phenolic products

The bio-oil obtained from the catalytic pyrolysis at bed-scale was characterised using GC/MS to investigate the effects of temperature and KOH contents on the yields of phenolic compounds. Table 7-4 shows the yields of the individual phenolic compounds obtained, while Figure 7-8 shows the yields of each phenols group obtained on addition of the different KOH contents.

7.3.4.4.1. Effect of temperature and catalyst content on the total yield of phenols

Based on Table 7-3, only temperature had a pronounced influence on the yields of total phenols, with p-values of 0.07, while catalyst content had minimal influence, with p-value of 0.82. The associated negative coefficients for temperature factor (-

0.22) is an indication that temperature had a reducing effect on the yield of total phenols (Table 7-3). From Table 7-4, the conversion of lignin without catalyst, pyrolysed at 450 ^{o}C and 550 ^{o}C produced almost the same yield of total phenols (2.84 wt.% and 2.88 wt.%) respectively. On addition of the various KOH contents, the yields of total phenols obtained at 450 ^{o}C with 4.5 wt.% and 8.5 wt.% were both increased to 3.58 wt.% (maximum yield), equivalent to 26%. Similarly, pyrolysis at 550 ^{o}C with 4.5 wt.% and 8.5 wt.% KOH contents increased the yields to 2.98 wt.% and 3.16 wt.%, equivalent to 3% and 10% respectively. Hence, more pronounced catalytic effect was observed at relatively low temperature: The total phenols yield was maximised at lower temperature and KOH content than at higher temperature and higher KOH content. The influence of temperature and catalyst content is also illustrated in Figure 7-7. The highest yields of phenols are obtained at temperatures lower than 500 °C. The decrease in the optimum temperature, when compared to non-catalytic pyrolysis [40], is due to the lowering of the activation energy of some reactions breaking bonds between monomer units, resulting in enhanced depolymerisation. Compared to the total yields of phenols obtained using the TGA-TD-GC-MS with or without catalyst, as shown in Table 7-1, the yields obtained at bench scale were found to be significantly lower. This is probably due to the differences in reactor configuration, known to have significant influence on the phenolic yield distributions from lignin pyrolysis [41]. Furthermore, repolymerisation of the monomeric phenols in the bio-oil generated during bench-scale fast pyrolysis might have occurred [15]. Another possible phenomenon could be the occurrence of recombination reactions following condensation in liquid phase, leading to the formation of oligomers, which are not detected by the GC/MS [15]. Literature reports have shown that the introduction of hydrogen donating agents such as isopropyl

alcohol, methanol, formic acids, etc., during lignocellulosic fractionation have great influences on stabilisation of the generated reactive monomeric phenols [16,17,42]. Therefore, pyrolysis in the presence of hydrogen donating agents could be worthwhile.

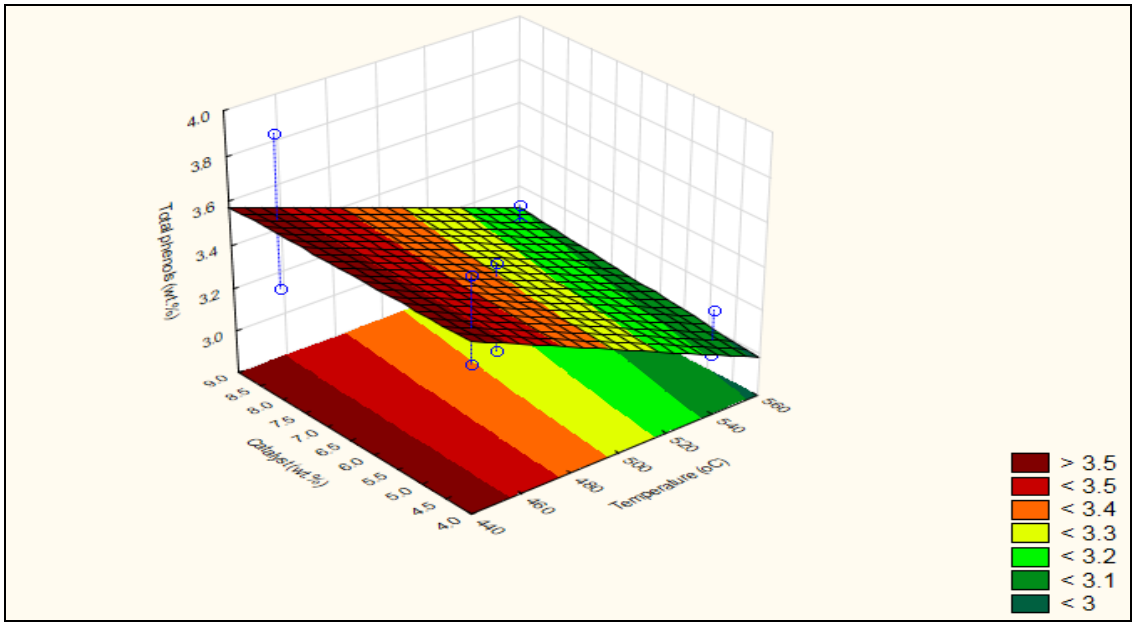

Figure 7-8: The response surface and contour lines of total phenols yield as a function of temperature and catalyst content

7.3.4.4.2. Effect of temperature and catalyst content on the yield of phenolic compounds

Regarding the yield of phenols groups classified as S-type, G-type and P-type phenols, considering the S-type phenols (Figure 7-8), the production decreased with increase in temperature, and KOH content as confirmed by the negative coefficients of -0.21 and -0.06 (Table not shown). Only the yields obtained at 450 ^{o}C with 4.5 wt.% and 8.5 wt.% were found to be statistically significant (p-value = 0.0013 and 0.031) respectively. At these two conditions, yield of S-type phenols were increased from 0.41 wt.% to 0.76 wt.% and 0.57 wt.%, equivalent to 85% and 37% increases respectively. At 550 ^{o}C with 4.5 wt.% and 8.5 wt.% KOH contents, the yields were

found to be not statistically significant (p-values of 0.28 and 0.47 respectively). Hence, the maximum amount of S-type phenols was obtained at 450 ^{o}C and 4.5 of KOH content. The production of more S-type phenols at lower temperature, due to the relatively low thermal stability of the methoxy groups, is consistent with literature report [40]. Among the S-type phenolic compounds (Table 7-4), syringol was the major product, of which pyrolysis at 450 ^{o}C with 4.5 wt.% and 8.5 wt.% significantly improved the yields from 0.34 wt.% to 0.70 wt.% and 0.53 wt.%, with p-values of 0.01 and 0.02 respectively. Again, the maximum amount (0.71 wt.%), equivalent to 106% increase was obtained at 450 ^{o}C with 4.5 wt.% KOH content, as compared to the non-catalytic yield (0.34 wt.%). A similar trend was observed with the pyrolysis at analytical scale using the TGA-TD-GC-MS, where syringol was the main quantified S-type compound.

Regarding the G-type phenols (Figure 7-8), the yields were significantly reduced with increase in temperature and KOH content, except for the pyrolysis at 450 ^{o}C/4.5 wt.% which significantly increased the yield from 1.51 wt.% to 1.68 wt.%, equivalent to 12% increase (p-value = 0.06). Among the G-type phenols, guaiacol was the main compound that was significantly produced (Table 7-4). Like the trend observed for syringol, the yield was maximised at 450 ^{o}C and 4.5 wt. % KOH content, with an increase of 0.62 wt.%, equivalent to 83% (p-value of 0.004), as compared to the non-catalytic yield (0.34 wt.%). Therefore, the production of both S-type and G-type phenols requires low temperature depolymerisation and relatively low catalyst content.

For the P-type phenols (Figure 7-8), the yields obtained on pyrolysis without catalyst at 450 ^{o}C and 550 ^{o}C produced were 0.96 wt.% and 1.50 wt.% respectively. These results are consistent with literature, as pyrolysis at higher temperature usually

generated more P-type phenols than pyrolysis at lower temperatures [33,43]. This is due to increased conversion of the lignin substituents as evident by the higher amount of gases obtained at 550 ºC than at 450 ºC (Figure 7-3). On addition of the various contents of KOH (Figure 7-8), only the pyrolysis at 450 ºC with 8.5 wt.% KOH content significantly increased the yields from 0.92 wt.% to 1.63 wt.%, equivalent to 77% (p-value of 0.07). The major P-type phenol produced in higher yield was phenol (Table 7-4), of which the production reached a maximum of 0.96 wt.% (141% increase) at 450 ºC and KOH content of 8.5 wt.% (p-value = 0.034).

Overall, the production of the three classes of phenolic compounds were maximised at the reaction temperature of 450 ºC, of which the yields of the S-type and G-type phenols reached their maxima with 4.5 wt.% KOH content, and the P-type phenols with 8.5 wt.% KOH content.

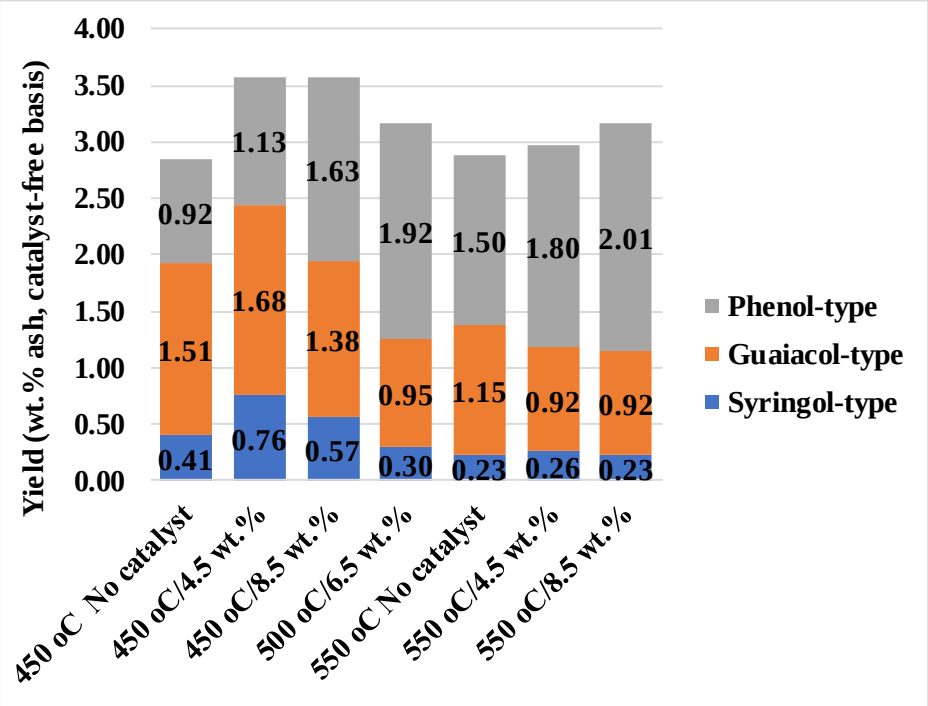

Figure 7-9: Yields of Syringol-type, Guaiacol-type, and Phenol-type phenols obtained by GC/MS analysis of bio-oil from the catalytic pyrolysis of SD lignin

Table 7-4 Yields of monomeric products (wt.%, ash, catalyst-free basis) by GC/MS analysis of bio-oil from the catalytic pyrolysis of SD lignin

Compounds	450 ºC No catalyst	450 ºC 4.5 wt.%	450 ºC 8.5 wt.%	500 ºC 6.5 wt.%	550 ºC No catalyst	550 ºC 4.5 wt.%	550 ºC 8.5 wt.%
Syringol-type							
Syringol	0.34	0.71	0.52	0.26	0.17	0.22	0.20
Acetosyringone	0.07	0.06	0.04	0.04	0.06	0.04	0.03
Sum	**0.41**	**0.76**	**0.57**	**0.30**	**0.23**	**0.26**	**0.23**
Guaiacol-type							
Guaiacol	0.34	0.62	0.52	0.28	0.22	0.23	0.24
creosol	0.22	0.08	0.05	0.03	0.12	0.02	0.02
4-ethylguaiacol	0.21	0.15	0.11	0.06	0.11	0.06	0.05
4-vinylguaiacol	0.49	0.56	0.45	0.41	0.46	0.41	0.39
4-propylguaiacol	0.01	0.02	0.01	0.00	0.01	0.00	0.00
trans-isoeugenol	0.20	0.23	0.22	0.16	0.19	0.20	0.21
Vanillin	0.03	0.02	0.02	0.01	0.04	0.00	0.00
Sum	**1.51**	**1.68**	**1.38**	**0.95**	**1.15**	**0.92**	**0.92**
Phenol-type							
Phenol	0.40	0.71	0.96	1.02	0.54	0.90	1.06
o-cresol	0.05	0.08	0.16	0.21	0.09	0.18	0.22
2,6-dimethylphenol	0.00	0.01	0.03	0.04	0.02	0.03	0.04
p+m-cresol	0.16	0.11	0.19	0.22	0.25	0.19	0.25
2,4-xylenol	0.03	0.03	0.08	0.09	0.07	0.09	0.09
4-ethylphenol	0.30	0.19	0.21	0.25	0.35	0.24	0.26
Catechol	0.00	0.00	0.00	0.10	0.18	0.17	0.09
Sum	**0.92**	**1.13**	**1.63**	**1.92**	**1.50**	**1.80**	**2.01**
Total Phenols	**2.84**	**3.58**	**3.58**	**3.17**	**2.88**	**2.98**	**3.16**

7.4. Conclusion

Optimisation of phenols production from soda lignin using KOH as the catalyst was investigated both at analytical and at bench scales to maximise the yields of phenolic

products. From the results at analytical scale, the total phenols yields were increased up to 5.3 wt.% and 16.0 wt.% using 5 and 7 wt.% KOH contents respectively. At bench-scale, the highest total phenols yields were much lower (3.6 wt.%) than that of analytical scale, attributed to the difference in reactor configuration as well as the enhancement of repolymerisation reactions. The main phenolic compounds obtained in significant amounts from the analysis of the bio-oil from the bench-scale were syringol, guaiacol, and phenol. The highest yields were 0.7wt.%, 0.62 wt.%, and 0.96 wt.% obtained at 450 ^{o}C/4.5 wt.% (syringol and guaiacol), and 450 ^{o}C/8.5 wt.% (phenol), which represented about 106%, 83%, and 141% increases respectively, compared with the non-catalytic yields. Overall, the optimisation of phenols production from soda lignin pyrolysis required relatively low temperature (450 ^{o}C) due to the lowering of the activation energy of some reactions breaking bonds between monomer units, resulting in enhanced depolymerisation in presence of catalyst.

7.5. Reference

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CHAPTER EIGHT

CONCLUSIONS AND RECOMMENDATIONS

This chapter summarises the overall conclusions drawn from this research work, and the recommendations for further improvements of lignin pyrolysis technology in the future. The overall idea of this dissertation was to maximise the yield of phenols by investigation of the influence of catalysts on different lignin types.

In this study, several technical lignins were considered. As lignins from different plant origins and isolation techniques have different compositions, with the goal to better understand the mechanism of conversion, an extensive characterisation of the lignin samples was essential. Characterisation was done by elemental and proximate analyses, FTIR, GPC and several wet chemical methods including thioacidolysis. In the context of this screening study, a mg scale method was adapted in order to investigate the potential of 12 catalysts on 3 different types of lignins for phenols production. This was done by TGA-TD-GC/MS, a method recently developed for the analysis of lignocellulosic biomass at Stellenbosch University. In order to study lignin conversion, the instrument was calibrated for quantification of 27 phenols. From the different lignin samples, the yields of typical monomeric phenols produced was within the range of 5.5-11.2 wt.% of the lignin mass. In order to assess the method, H:G:S ratios were compared, and were found to be consistent with the type of feedstock (softwood, hardwood or non-woody) and very similar for samples from a same plant material. Due to the catalytic cracking effect of the inorganic elements, the TGA-TD-GC/MS was found to be effective for the lignins of high purity (amounts of ash less than 5%). A drawback of this method is that the lignin reproducibility was found to be lower than with lignocellulose biomass. This could be due to the tendency

of phenols to recombine and condense, resulting in partial obstruction of some pipes in the thermal desorber, or formation of heavy compounds in the TD tubes, that cannot be volatilised for GC/MS analysis. For future tests, the use of smaller sample size would be recommended.

A comparative study of monomeric phenols production from the catalytic pyrolysis of hardwood (eucalyptus), softwood (pine), and herbaceous (sugarcane bagasse) lignins using four catalysts showed that the catalysts, especially the hydroxides displayed more pronounced catalytic effects on eucalyptus and sugarcane bagasse lignins than on pine lignin. This was attributed to the presence of less oxygenated linkages and more C-C bonds in the monomeric units of softwood lignin. Potassium hydroxide had the highest influence on the yield of total phenols from the sugarcane bagasse lignin, leading to a yield increase of +26%, and likewise sodium hydroxide from eucalyptus lignin (+40%). This was attributed to a more intimate contact of these hydroxide catalysts with the lignin during impregnation than with the metal oxides catalysts. The yields of some valuable phenolic compounds were also increased by these hydroxides. Especially, the KOH increased the yield of 4-vinylguaiacol up to 2.80 wt.%, equivalent to 39% increase from sugarcane bagasse lignin, while NaOH increased the yield of syringol from *E. grandis* up to 1.8 wt.%, equivalent to 90 % increase, as compared to the pyrolysis yields without catalysts. The production of these syringol-type and guaiacol-type phenols by the hydroxides was likely correlated with the increased intensities of their respective DTG signals below 350 ^{o}C. With the metal oxides, their selectivities towards the production of syringol-type and guaiacol-type phenols were limited. They were more selective towards the production of phenol-type phenols through the demethoxylation of the syringol-type and guaiacol-type phenols. In particular, ZnO promoted the demethoxylation reactions from sugarcane

bagasse lignin, leading to a yield increase from 2.13 wt.% for the non-catalytic yield to 2.96 wt.%, equivalent to 36%.

As the highest yields of phenols were obtained with sugarcane bagasse lignin, this material was selected for further screening of three isolation processes and 12 catalysts. This provided insight into the selection of the best performing catalysts that could be considered for further investigation for maximisation of phenols production. Most of the catalysts enhanced depolymerisation reactions at lower temperature (<350 ^{o}C), with KOH and CaO producing the most effects on the production of primary phenolic products (syringol-type and guaiacol-type). The main compounds were syringol, guaiacol, and 4-vinyguaiacol with significant yields within the range of 0.5-2.8 wt.%. In comparison with yields obtained from non-catalytic conversion, yields increase equivalent to 32-120% were obtained. Due to the promotion of demethoxylation reactions by ZnO, NaOH, and CaO respectively, the yield of phenol, as the main phenol-type compound was within the range of 0.9-1.8 wt.%, equivalent to 39-58%, as compared to the non-catalytic yields. These significant increases in the yields of phenols using 1 wt.% compared to ≥ 10 wt.% reported in literatures demonstrated the effectiveness of impregnation method.

Informed by the relatively high yield of phenolic compounds obtained in previous works from soda lignin with KOH, an investigation of optimisation of phenols production was ensued, firstly, by assessing the influence of the catalyst content on the yields of phenols at analytical (milligram) scale. The results showed that the maximum yields of phenolic compounds were obtained using 5 wt.% and 7 wt.% KOH contents (15.3 wt.% and 16.0 wt.% respectively). Based on these results, fast pyrolysis was then conducted at bench (gram) scale, focussing on the effects of catalyst amounts and temperatures (450-550 ^{o}C) to determine the optimum conditions.

Fast pyrolysis was considered as it is known to generate much higher bio-oil yield than slow pyrolysis. The analysis of the bio-oil obtained showed that the yields of syringol and guaiacol had their maximum values at 450 ^{o}C and 4.5 wt.% KOH content (0.70 wt.% and 0.6 wt.%,), representing 106% and 83% increases respectively. Similarly, the production of lower molecular weight (P-type) phenols were maximised at lower temperature (450 ^{o}C), but at higher KOH content (8.5 wt.%), with phenol as the main compound, possibly promoted by demethoxylation reactions. Overall, fast pyrolysis yields at bench scale resulted in remarkably lower yields of phenolic products than the ones obtained at analytical scale, attributed to differences in reactor type. Another reason could be that repolymerisation of the reactive monomeric phenols formed during the catalytic pyrolysis at bench scale might have occurred. Therefore, a further improvement in the yields could be advanced by conducting pyrolysis in the presence of hydrogen-donor agents such as formic acid, hydrogen gas, isopropyl alcohol methanol, etc. This has been exemplified in recent time through reductive catalytic fractionation (RCF) processes of whole lignocellulose with the use of hydrogen gas and isopropyl alcohol, formaldehyde. This could have the advantage of providing an *in situ* source of hydrogen to stabilise the phenolic monomers generated during pyrolysis, and thus inhibits repolymerisation reactions.

Finally, in this research work, the approach consisted in impregnating the catalysts with lignin. Following pyrolysis, the metal catalyst remained in the char residues. Although relatively cheap catalysts were used, further research can be conducted on the recovery and reuse of these catalysts, to improve the economic viability of the process. In addition to this, analysis of chars by NMR could help better understand mechanisms of catalytic conversion of these lignins.

Appendices

Appendix A: Results related to Chapter 4

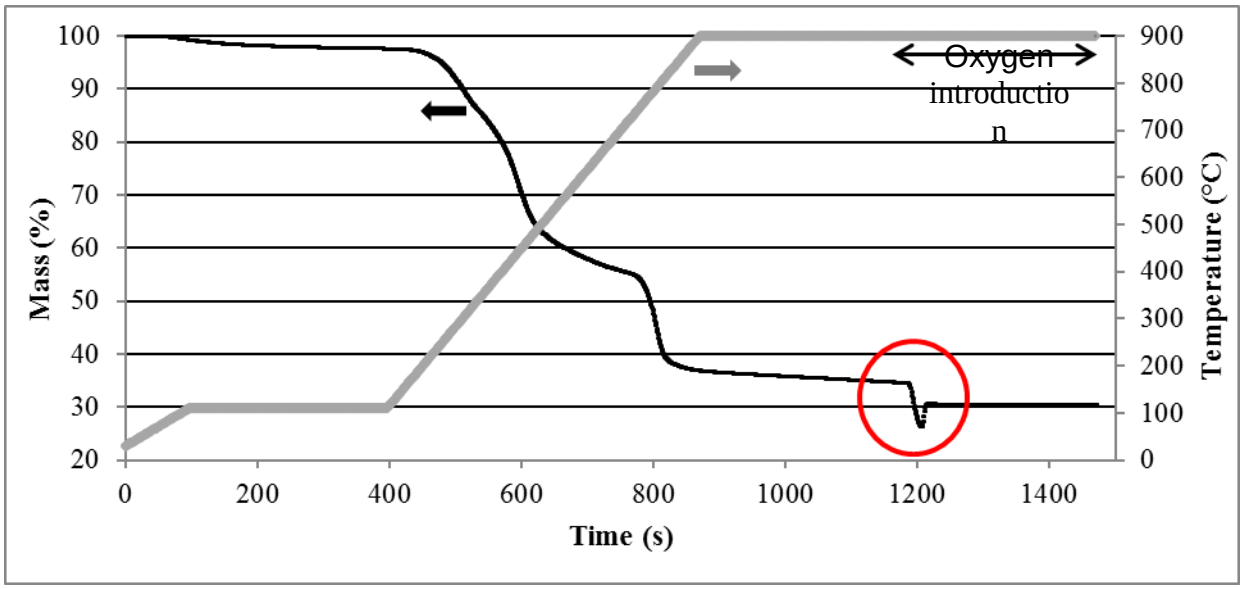

Figure A-1: Thermogravimetric analysis of PE-K-M lignin sample showing a mass increase during the combustion step of the proximate analysis due to inorganics oxidation.

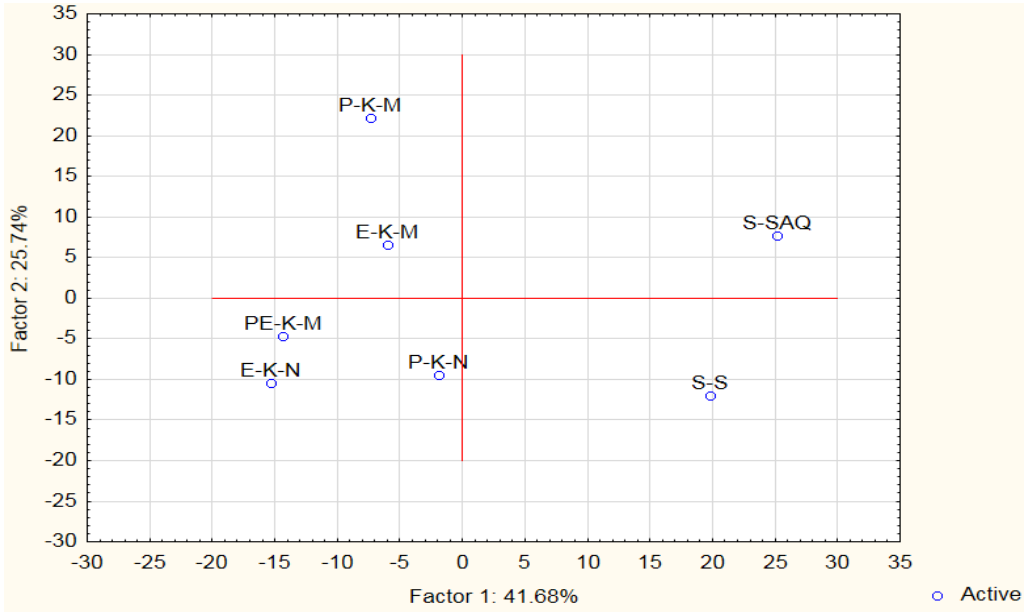

Figure A-2: Principal Component Analysis (PCA) Score Plots on Factors 1 and 2 (PCA 1 and PCA 2) based on Fourier Transform Infra-Red analysis of the lignins

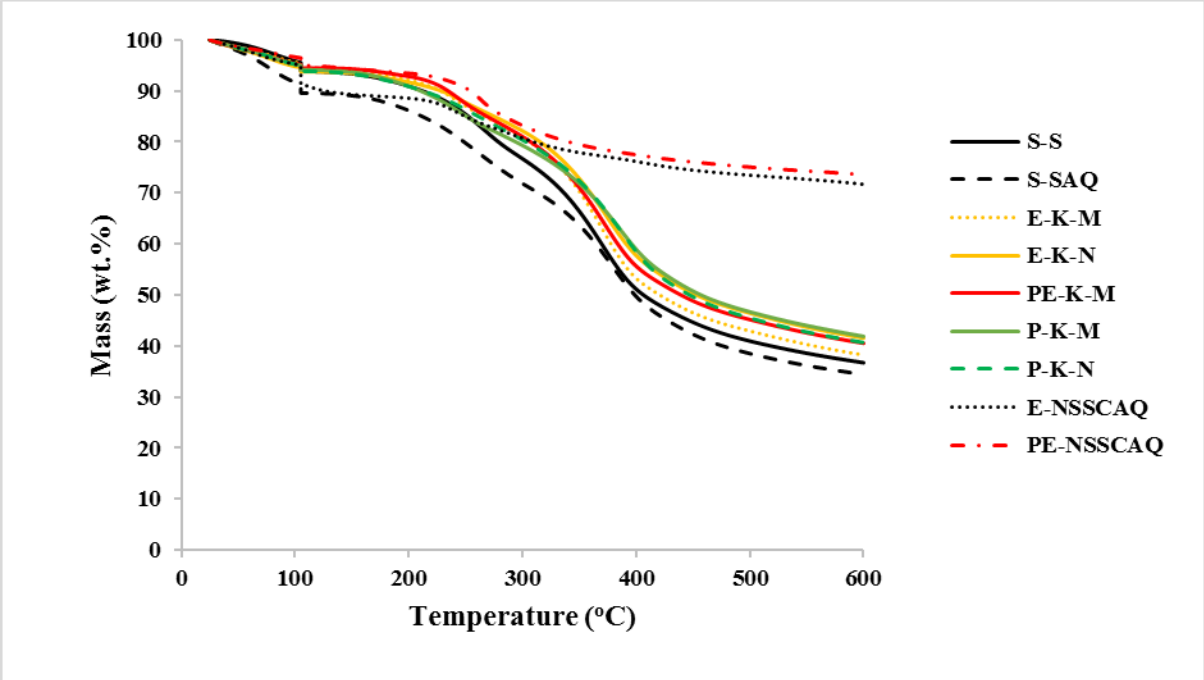

Figure A-3: TGA Curves of Purified Lignins and Dried Sulphite Spent Liquors (E-NSSCAQ and PE-NSSCAQ) Obtained Under the Heating Rate of 10 °C/min.

Appendix B: Results Related to Chapter Five

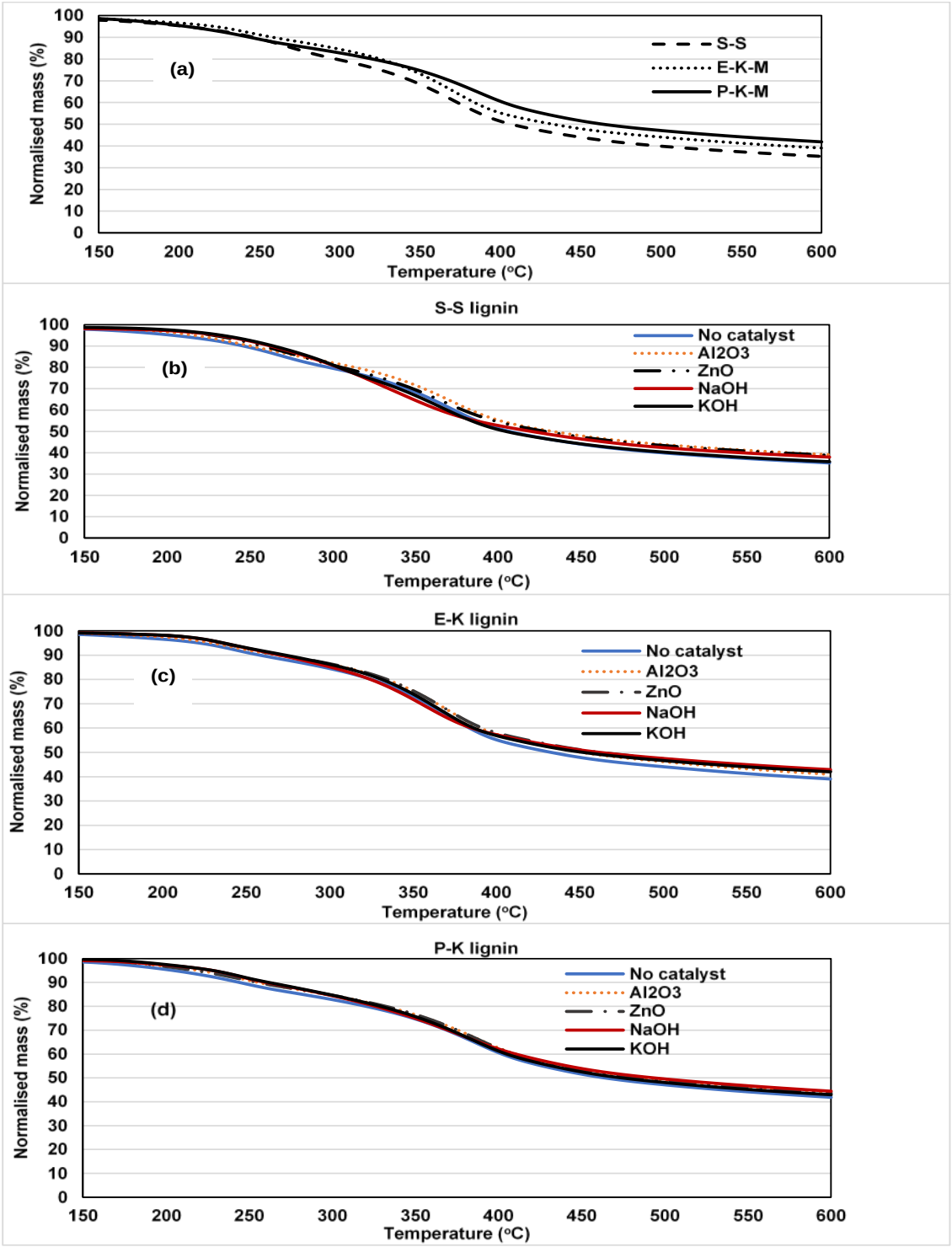

Figure B-8a-d. TGA Curves of Lignin Pyrolysis Without Catalyst (a) and With Catalysts (b) for S-S, (c) for E-K, and (d) for P-K Lignins Obtained Under the Heating Rate of 10 ºC/min.

Appendix C: Results related to Chapter 6

Table C-1: Yields of monomeric products (wt.% dry, ash, catalyst-free basis) from catalytic pyrolysis of SD lignin

Compound	No catalyst	Al_2O_3	Ni-Al_2O_3-SiO_2	NiO	CaO	CuO	Fe_2O_3	MgO	MoO_3	ZnO	NaOH	KOH	TiO_2
C_0 phenols													
Syringol	0.68	0.70	0.72	0.69	0.63	0.52	0.71	0.60	0.58	0.64	0.87	0.96	0.62
Guaiacol	1.06	1.29	1.27	1.19	1.07	0.76	1.15	1.04	0.96	1.24	0.55	1.40	0.75
Phenol	1.28	1.66	1.52	1.39	1.23	1.18	1.58	1.27	1.17	1.79	1.44	1.54	1.35
o-cresol	0.75	0.94	0.77	0.76	0.70	0.60	0.88	0.72	0.57	0.99	0.75	0.83	0.76
Sum	**3.78**	**4.59**	**4.27**	**4.04**	**3.62**	**3.06**	**4.32**	**3.63**	**3.29**	**4.66**	**3.62**	**4.73**	**3.48**
C_1 phenols													
4-methylanisole	0.12	0.16	0.15	0.14	0.12	0.10	0.14	0.12	0.10	0.18	0.13	0.13	0.12
4-methylsyringol	0.47	0.47	0.53	0.46	0.42	0.35	0.49	0.45	0.46	0.43	0.24	0.58	0.43
creosol	0.50	0.59	0.66	0.56	0.45	0.43	0.55	0.49	0.53	0.58	0.29	0.59	0.50
p+m-cresol	0.73	0.90	0.87	0.75	0.57	0.59	0.87	0.64	0.72	0.94	0.50	0.78	0.77
2,4-xylenol	0.11	0.13	0.12	0.11	0.09	0.08	0.13	0.09	0.09	0.15	0.09	0.12	0.12
Sum	**1.92**	**2.25**	**2.32**	**2.01**	**1.65**	**1.56**	**2.18**	**1.79**	**1.89**	**2.27**	**1.26**	**2.21**	**1.93**
C_2 phenols													
Acetosyringone	0.16	0.16	0.18	0.16	0.17	0.13	0.20	0.17	0.16	0.11	0.13	0.22	0.15
4-ethylguaiacol	0.23	0.38	0.36	0.27	0.26	0.23	0.33	0.31	0.25	0.35	0.25	0.32	0.29
4-vinylguaiacol	2.01	1.40	2.25	1.94	1.85	1.29	1.74	1.59	1.59	2.29	1.79	2.80	1.47
Acetoguaiacone	0.08	0.09	0.10	0.08	0.09	0.08	0.10	0.10	0.09	0.08	0.07	0.11	0.08
4-ethylphenol	0.34	0.52	0.48	0.37	0.29	0.30	0.44	0.35	0.37	0.52	0.28	0.40	0.42
Sum	**2.82**	**2.55**	**3.36**	**2.82**	**2.67**	**2.03**	**2.81**	**2.51**	**2.45**	**3.35**	**2.51**	**3.86**	**2.41**
C_3 phenols													
Isoeugenol	0.22	0.21	0.24	0.22	0.25	0.21	0.23	0.24	0.21	0.23	0.24	0.28	0.21
Others													
Anisole	0.14	0.21	0.23	0.17	0.16	0.15	0.23	0.19	0.18	0.03	0.16	0.10	0.16
Toluene	0.29	0.33	0.33	0.29	0.27	0.24	0.34	0.29	0.40	0.35	0.30	0.32	0.28
Furfural	1.88	4.55	2.93	2.44	0.86	2.03	3.12	1.72	2.37	2.44	0.43	1.57	2.88
Total phenols yield	**8.74**	**9.60**	**10.18**	**9.08**	**8.19**	**6.86**	**9.54**	**8.17**	**7.84**	**10.50**	**7.63**	**11.07**	**8.03**

Table C-2: Yields of monomeric products (wt.% dry, ash, catalyst-free basis) from catalytic pyrolysis of SAQ lignin

Compound	No catalyst	Al_2O_3	Ni-Al_2O_3-SiO_2	NiO	CaO	CuO	Fe_2O_3	MgO	MoO_3	ZnO	NaOH	KOH	TiO_2
C_0 phenols													
Syringol	0.28	0.37	0.42	0.40	0.55	0.41	0.36	0.43	0.33	0.22	0.62	0.53	0.40
Guaiacol	0.57	0.61	0.76	0.72	1.04	0.75	0.73	0.74	0.62	0.48	1.10	0.78	0.68
Phenol	0.73	0.78	0.91	0.81	1.12	0.91	1.01	0.89	0.78	0.67	0.99	0.80	0.87
o-cresol	0.47	0.50	0.49	0.42	0.66	0.53	0.60	0.53	0.42	0.39	0.52	0.41	0.53
3-methoxycatechol	0.27	0.33	0.38	0.32	0.28	0.28	0.27	0.36	0.28	0.24	0.37	0.38	0.31
Sum	**2.33**	**2.60**	**2.96**	**2.66**	**3.65**	**2.88**	**2.98**	**2.96**	**2.43**	**2.01**	**3.60**	**2.89**	**2.78**
C_1 phenols													
4-methylanisole	0.05	0.06	0.09	0.07	0.09	0.07	0.07	0.07	0.06	0.07	0.08	0.06	0.06
4-methylsyringol	0.23	0.29	0.33	0.31	0.37	0.30	0.28	0.36	0.25	0.18	0.29	0.36	0.29
creosol	0.33	0.39	0.48	0.42	0.55	0.42	0.41	0.46	0.36	0.27	0.41	0.42	0.40
Vanillin	0.06	0.08	0.10	0.08	0.11	0.08	0.09	0.10	0.05	0.05	0.10	0.10	0.08
p+m-cresol	0.46	0.50	0.59	0.49	0.68	0.56	0.63	0.56	0.52	0.39	0.49	0.45	0.53
2,4-xylenol	0.08	0.08	0.08	0.06	0.10	0.08	0.09	0.08	0.07	0.06	0.07	0.06	0.08
Sum	**1.20**	**1.39**	**1.66**	**1.43**	**1.91**	**1.51**	**1.57**	**1.63**	**1.31**	**1.01**	**1.45**	**1.44**	**1.44**
C_2 phenols													
Acetosyringone	0.12	0.14	0.18	0.17	0.20	0.16	0.11	0.20	0.15	0.10	0.21	0.21	0.15
4-ethylguaiacol	0.16	0.20	0.26	0.23	0.29	0.24	0.25	0.24	0.21	0.16	0.28	0.25	0.25
4-vinylguaiacol	0.74	0.80	1.03	0.78	1.36	0.70	0.80	1.11	0.63	0.66	1.17	1.10	0.63
Acetoguaiacone	0.07	0.07	0.08	0.07	0.09	0.08	0.08	0.08	0.07	0.06	0.08	0.09	0.07
4-ethylphenol	0.22	0.26	0.34	0.30	0.35	0.31	0.33	0.31	0.30	0.21	0.31	0.29	0.33
Sum	**1.31**	**1.48**	**1.90**	**1.56**	**2.30**	**1.49**	**1.57**	**1.94**	**1.37**	**1.19**	**2.06**	**1.95**	**1.42**
C_3 phenols													
Isoeugenol	0.21	0.20	0.20	0.20	0.22	0.19	0.20	0.21	0.19	0.20	0.21	0.21	0.19
Others													
Anisole	0.10	0.14	0.20	0.12	0.16	0.13	0.17	0.16	0.17	0.18	0.13	0.10	0.13
Toluene	0.12	0.13	0.15	0.13	0.16	0.16	0.18	0.14	0.23	0.10	0.14	0.12	0.14
Furfural	4.29	4.87	6.00	7.05	2.62	6.76	6.17	3.57	5.71	3.36	1.51	3.35	7.87
Total phenols yield	**5.06**	**5.67**	**6.72**	**5.84**	**8.08**	**6.07**	**6.31**	**6.74**	**5.29**	**4.41**	**7.32**	**6.50**	**5.83**

Table C-3: Yields of monomeric products (wt.% dry, ash, catalyst-free basis) from catalytic pyrolysis of SEH lignin

Compound	No catalyst	Al_2O_3	Ni-Al_2O_3-SiO_2	NiO	CaO	CuO	Fe_2O_3	MgO	MoO_3	ZnO	NaOH	KOH	TiO_2
C_0 phenols													
Syringol	0.43	0.44	0.47	0.48	0.48	0.53	0.61	0.43	0.55	0.31	0.74	0.64	0.57
Guaiacol	0.77	0.78	0.85	0.86	0.96	0.94	1.11	0.81	0.95	0.62	1.36	1.23	0.95
Phenol	0.87	0.85	0.87	0.89	1.12	0.94	1.22	0.98	1.04	0.81	1.38	1.27	1.01
o-cresol	0.46	0.41	0.38	0.42	0.57	0.44	0.59	0.50	0.48	0.41	0.75	0.62	0.53
Sum	**2.54**	**2.48**	**2.57**	**2.64**	**3.12**	**2.85**	**3.52**	**2.71**	**3.02**	**2.16**	**4.23**	**3.77**	**3.07**
C_1 phenols													
4-methylanisole	0.11	0.11	0.13	0.12	0.17	0.13	0.17	0.16	0.13	0.15	0.18	0.17	0.13
4-methylsyringol	0.28	0.30	0.34	0.32	0.31	0.35	0.42	0.31	0.48	0.24	0.19	0.17	0.34
creosol	0.34	0.36	0.39	0.38	0.41	0.43	0.49	0.37	0.56	0.30	0.22	0.20	0.45
Vanillin	0.04	0.08	0.05	0.05	0.06	0.06	0.06	0.05	0.07	0.05	0.04	0.04	0.05
p+m-cresol	0.56	0.56	0.47	0.52	0.72	0.61	0.84	0.65	0.88	0.57	0.53	0.42	0.61
2,4-xylenol	0.08	0.07	0.05	0.06	0.10	0.07	0.11	0.09	0.10	0.08	0.10	0.07	0.08
Sum	**1.41**	**1.49**	**1.43**	**1.45**	**1.76**	**1.65**	**2.09**	**1.63**	**2.22**	**1.39**	**1.26**	**1.06**	**1.65**
C_2 phenols													
Acetosyringone	0.06	0.06	0.07	0.06	0.07	0.08	0.08	0.06	0.09	0.05	0.06	0.05	0.07
4-ethylguaiacol	0.11	0.10	0.10	0.10	0.11	0.11	0.13	0.10	0.12	0.09	0.12	0.10	0.11
4-vinylguaiacol	1.33	1.48	1.46	1.50	1.75	1.66	2.00	1.63	2.01	1.36	1.53	1.33	1.62
Acetoguaiacone	0.06	0.06	0.06	0.06	0.07	0.07	0.07	0.07	0.08	0.06	0.06	0.05	0.06
4-ethylphenol	0.15	0.15	0.13	0.14	0.17	0.16	0.20	0.16	0.20	0.14	0.16	0.13	0.16
Sum	**1.71**	**1.85**	**1.83**	**1.86**	**2.17**	**2.07**	**2.49**	**2.02**	**2.50**	**1.71**	**1.94**	**1.65**	**2.01**
C_3 phenols													
4-allylsyringol	0.04	0.04	0.04	0.04	0.04	0.05	0.05	0.04	0.05	0.03	0.03	0.03	0.04
Isoeugenol	0.25	0.31	0.26	0.25	0.26	0.27	0.28	0.26	0.27	0.24	0.24	0.23	0.25
Sum	**0.28**	**0.35**	**0.30**	**0.30**	**0.30**	**0.32**	**0.34**	**0.30**	**0.32**	**0.28**	**0.27**	**0.26**	**0.30**
Others													
Anisole	0.10	0.12	0.13	0.12	0.17	0.13	0.18	0.17	0.21	0.19	0.15	0.13	0.12
Toluene	0.22	0.27	0.23	0.24	0.31	0.25	0.36	0.28	0.56	0.22	0.31	0.26	0.25
Furfural	0.20	0.16	0.22	0.24	0.22	0.26	0.30	0.24	0.37	0.25	0.15	0.14	0.25
Total phenols yield	**5.93**	**6.16**	**6.14**	**6.25**	**7.35**	**6.89**	**8.45**	**6.66**	**8.08**	**5.54**	**7.70**	**6.75**	**7.03**

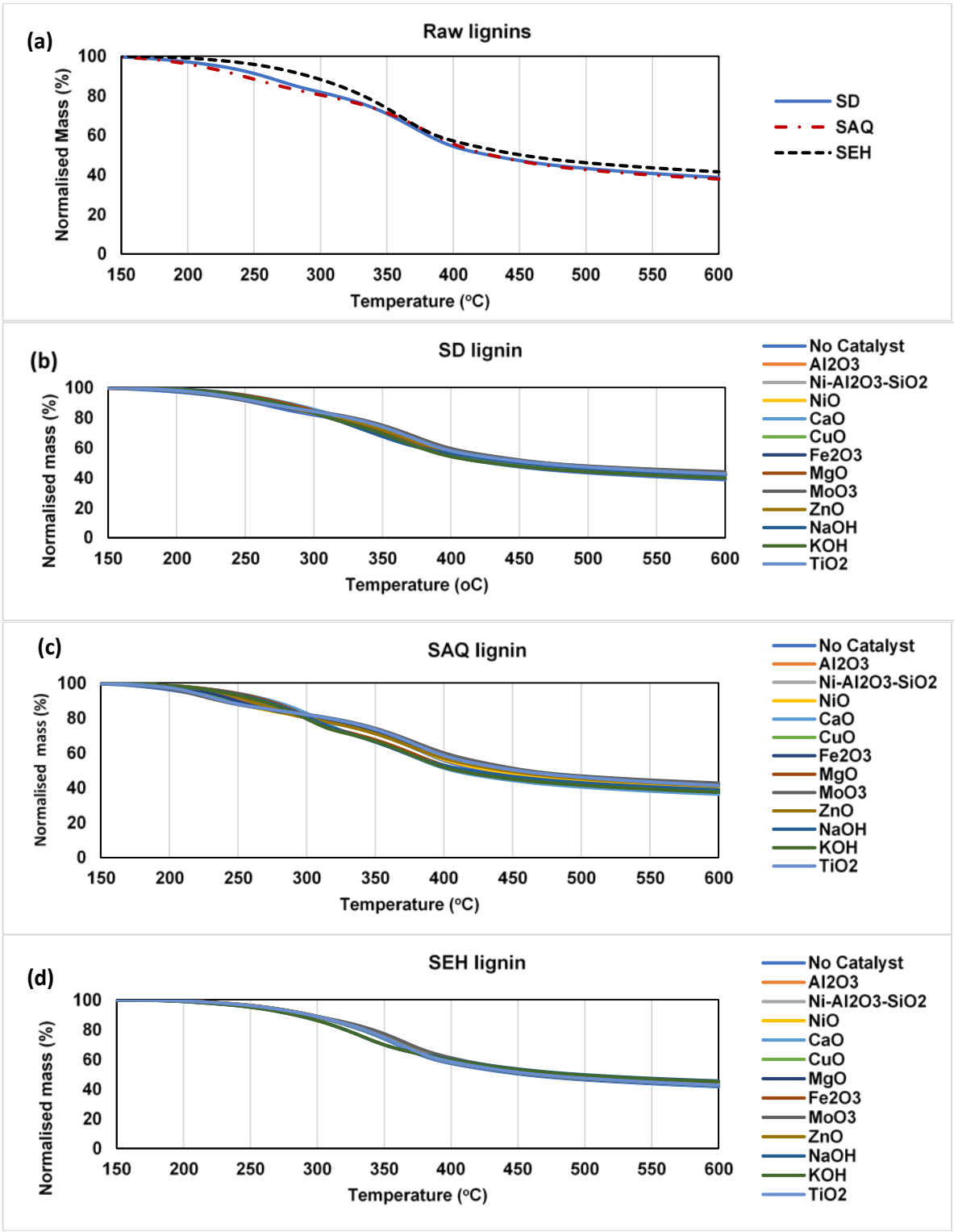

Figure C-1: TG curves of raw lignin (a), catalytic pyrolysis of SD lignin (b), SAQ lignin (c), and SEH lignin (d).